View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by Works

Swarthmore College

Works

Chemistry & Biochemistry Faculty Works

Chemistry & Biochemistry

3-15-1991

Nonadiabatic Electronic Interactions In The Ion-Pair States Of NeICl

Thomas Alex Stephenson
Swarthmore College, tstephe1@swarthmore.edu

Y. Hong

M. I. Lester

Follow this and additional works at: https://works.swarthmore.edu/fac-chemistry

Part of the Physical Chemistry Commons

Let us know how access to these works benefits you

Recommended Citation

Thomas Alex Stephenson, Y. Hong, and M. I. Lester. (1991). "Nonadiabatic Electronic Interactions In The Ion-Pair States Of NeICl". *Journal Of Chemical Physics*. Volume 94, Issue 6. 4171-4181. DOI: 10.1063/1.460650
https://works.swarthmore.edu/fac-chemistry/12

This work is brought to you for free and open access by . It has been accepted for inclusion in Chemistry & Biochemistry Faculty Works by an authorized administrator of Works. For more information, please contact myworks@swarthmore.edu.

AIP | The Journal of Chemical Physics

Nonadiabatic electronic interactions in the ionpair states of NeICl

Thomas A. Stephenson, Yujian Hong, and Marsha I. Lester

Citation: The Journal of Chemical Physics **94**, 4171 (1991); doi: 10.1063/1.460650
View online: http://dx.doi.org/10.1063/1.460650
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/94/6?ver=pdfcov
Published by the AIP Publishing

AIP Publishing Re-register for Table of Content Alerts

Create a profile. Sign up today!

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.58.64.71 On: Sat, 30 Nov 2013 17:30:00

Nonadiabatic electronic interactions in the ion-pair states of NeICl

Thomas A. Stephenson
Department of Chemistry, Swarthmore College, Swarthmore, Pennsylvania 19081
Yujian Hong and Marsha I. Lester
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

(Received 11 October 1990; accepted 12 December 1990)

Nonadiabatic interactions in the NeICl van der Waals complex have been explored in the lowest energy triad of ICl ion-pair states ($\sim$39 000 cm^{-1}). Dispersed fluorescence measurements reveal emission characteristic of multiple ion-pair electronic states, with the relative contributions from the $E(0^+)$, $\beta(1)$, and $D'(2)$ states changing with the initial ICl vibrational excitation (v_{ICl}). Emission directly from NeICl ($v_{\text{ICl}} = 0$) complexes indicates that the initially prepared NeICl levels have mixed electronic character and that the ICl electronic parentage changes with the initial van der Waals vibrational level selected. NeICl complexes prepared with 1–4 quanta of ICl stretch undergo rapid vibrational predissociation with a strong propensity for $\Delta v_{\text{ICl}} = -1$ relaxation. The electronic state(s) populated in the ICl fragments differ from the mixed electronic character of the initially prepared level, demonstrating that vibrational predissociation is accompanied by nonadiabatic electronic state changing processes. The observed final state selectivity may be attributed to the relative strength of the nonadiabatic couplings between the initial NeICl bound state and the final ICl states or a momentum gap rationale based on the overlap between the NeICl bound state wave function and the highly oscillatory continuum wave function of the separating fragments.

I. INTRODUCTION

Theoretical and experimental studies of the spectroscopy and predissociation processes in rare gas/halogen triatomic van der Waals (vdW) molecules to date have focused on the intramolecular nuclear (i.e., rotational and vibrational) dynamics as a probe of the van der Waals interaction potential.[1-11] An implicit assumption in each of these studies has been that the rare gas atom represents only a negligible perturbation to the electronic wave function of the diatomic halogen/interhalogen molecule. Thus, the electronic character of the complex can be uniquely correlated to a single electronic state of the chemically bound diatomic halogen/interhalogen molecule. This idea is reflected by the predominate vocabulary of the field, in which the spectroscopic notation used for a given electronic state in the van der Waals complex is identical to that used for the diatomic molecule at infinite separation from the rare gas atom.

A number of experimental studies have indirectly suggested that such assumptions are not universally valid and that the presence of a rare gas atom may induce or enhance nonadiabatic couplings between diatomic halogen/interhalogen electronic states. For example, Levy and coworkers found that the intensity of ArI_2 fluorescence excitation features relative to those of uncomplexed iodine is a strong function of the B state vibrational level,[12] suggesting a competition between an electronic predissociation process (to form Ar + 2I) and vibrational predissociation (to form $\text{Ar} + \text{I}_2^*$) with a substantial vibrational dependence. This conjecture is supported by the direct absorbance measurements carried out by Atkinson and coworkers, in which the fluorescence quantum yield for ArI_2 varies from 0.50 for $v' = 21$ to 0.05 for $v' = 14$.[13] Similar mechanisms have been invoked to account for the absence of $B \leftarrow X$ HeCl_2 fluorescence excitation features associated with $v' \geqslant 26$,[4] as well as the complete absence of the $B \leftarrow X$ excitation spectrum in NeIBr.[14] In a theoretical calculation, Beswick and coworkers have proposed that nonadiabatic transitions may play a role in the photodissociation dynamics of rare gas-I_2 clusters, when excited above the $\text{I}_2 B$ state dissociation limit.[15]

The most direct demonstration of the importance of nonadiabatic electronic interactions in the dynamics of van der Waals complexes is found for the HgN_2 complex. In this study, Jouvet and Soep observed that excitation of HgN_2 to an electronic state correlating with $\text{N}_2 + \text{Hg}(^3P_1)$ leads to dissociation and the formation of a $^3P_0$ mercury atom.[16] Jouvet and Beswick carried out a detailed quantum mechanical study of this "fine-structure predissociation" in van der Walls complexes, with a focus on both atom–atom and atom–diatom complexes.[17] The electronic relaxation processes considered were limited, however, to those in which the fine structure state of the atomic constituent was changed.

Previous work in this laboratory (at the University of Pennsylvania) has focused on the vibrational predissociation dynamics of rare gas/ICl complexes upon excitation to both the $A(\Omega = 1)$ and $B(\Omega = 0^+)$ valence electronic states.[7,8] In these studies, a two-color pump-probe laser-induced fluorescence technique was utilized to first excite the complex to a particular vibrational level in the A or B electronic state, followed by a temporally delayed second laser which excited the ICl fragments produced in the vibrational predissociation of the complex to a higher energy ion-pair electronic state. Detection of total emission from the ion-pair state as a function of probe laser wavelength results in a fluorescence excitation spectrum that yields the quantum state distribution of the ICl photofragments. In addition, Drobits *et al.*[18] were able to demonstrate that the vibrational predissociation lifetime (τ_{vp}) of NeICl is sufficiently long

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.58.64.71 On: Sat, 30 Nov 2013 17:30:00

(3 ± 2 nanoseconds) for the $v = 14$ vibrational level in the A electronic state that when the two pulsed lasers are temporally overlapped, it is possible to directly excite NeICl to the ion-pair states in an optical–optical double resonance transition. The excitation spectrum revealed a number of bound levels in the NeICl van der Waals potential associated with the ICl ion-pair states.[9,18]

Consideration of the potential curves for the ICl ion-pair states (see Fig. 1) suggests that NeICl excited to these electronic states provides an opportunity to directly explore the importance of nonadiabatic interactions in rare gas/halogen complexes. The lowest energy group of ICl ion-pair states consists of three strongly bound ($D_e \approx 33\,500$ cm^{-1}) closely spaced electronic states all correlating with the ionic atoms I^+ ($^3P_2$) + Cl^- ($^1S_0$). These states are labeled, by convention, $E(\Omega = 0^+)$, $\beta(\Omega = 1)$, and $D'(\Omega = 2)$. Previous spectroscopic investigations have provided RKR potential energy curves for all three states (as plotted in Fig. 1) and have demonstrated the presence of weak J-dependent couplings between the β and E and between the β and D' electronic states.[22] Figure 1 also reveals that the spacing between electronic states is small compared to the vibrational interval in any single electronic state. Thus, the channels available to ICl fragments following vibrational predissociation of rare gas/ICl van der Waals complexes prepared in the ion-pair states include those that do not maintain the electronic character of the initially prepared state.

If NeICl assumes a linear equilibrium geometry in the ion-pair states, cylindrical ($C_{\infty v}$) symmetry is retained and Ω continues to be a well-defined quantum number for describing the electronic wave function in the complex. In this case, we expect three distinct potential energy curves (at the linear configuration) correlating with the β, E, and D' states of free Ne + ICl. We note that there is no *a priori* reason to expect that these three curves will be identical and anticipate that the possibility of varying van der Waals bond energies and shapes of the potential energy curves will result in differences in the dynamics of the complex. If NeICl assumes a nonlinear equilibrium geometry (C_s symmetry point group) in the ion-pair states, then the overall fivefold electronic degeneracy (arising ultimately from the $2J + 1 = 5$ degeneracy of the $I^+\ ^3P_2$ atomic state) of the system is completely lifted, and we expect, in principle, five distinct electronic potential energy surfaces, two each correlating with Ne + ICl(β) and Ne + ICl(D') and one correlating with Ne + ICl(E). Examples of the diversity of potential interactions that may arise is provided by the studies of the interactions between rare gas and open shell atoms. In both rare gas–O[23] and rare gas–Si complexes,[24] significant differences have been observed in both the well depths and range parameters for potentials correlating with degenerate spin–orbit states of the open shell atom. In Ar–Si, both attractive and repulsive van der Waals potentials have been found to correlate with the same Si spin–orbit state.[24] Further examples can be drawn from heavier systems such as the rare gas–Hg complexes.[25] The general problem of the representation of the interaction of "spherical" particles with open shell atoms has been treated by Aquilanti *et al.*[26] These examples of open shell atom–rare gas interactions strongly suggest that the NeICl potentials correlating with Ne and ICl in the β, E, and D' states may differ considerably from one another. Thus, the dynamics of NeICl upon excitation to the lowest-lying ion-pair states may be subject to a number of dramatic effects involving the interaction of a complex set of potential energy surfaces.

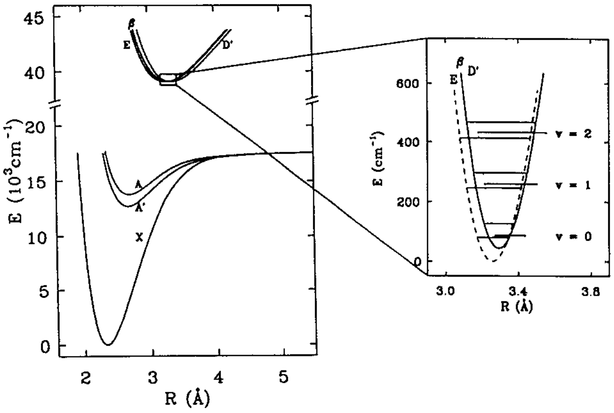

FIG. 1. RKR potential curves for the lowest lying valence and ion-pair electronic states of ICl. The insert shows an enlarged view of the $v = 0$–2 regions of the E, β, and D' ion-pair states. The RKR data for the X, A, and A' valence states and the ion-pair states are taken from Refs. 19–21 and 22, respectively.

The goal of the present investigation was to explore, using wavelength resolved emission, the electronic and vibrational character of the ICl fragments that resulted from vibrational predissociation of NeICl following excitation to the lowest energy triad of ICl ion-pair states. In a preliminary communication, we have described our results when we prepare complexes with one quantum of I–Cl stretching vibrational excitation ($v_{ICl} = 1$).[27] In this publication, we expand on our earlier work by presenting results from $v_{ICl} = 0$–4. At each level of vibrational excitation along the I–Cl coordinate, we observe direct evidence for nonadiabatic interactions induced by the presence of the Ne atom. Following a detailed presentation of our results in Sec. III, we discuss in Sec. IV some of the important issues that these experiments raise, along with a model that is consistent with our observations. A brief description of our experimental apparatus and procedures follows immediately in Sec. II.

II. EXPERIMENTAL

The investigations reported here were carried out on an apparatus at the University of Pennsylvania described in both our preliminary report[27] and in previous publications from this laboratory.[7,9] Briefly, NeICl van der Waals complexes were formed in a continuous expansion of ICl (Sigma) and first-run grade Ne (Airco) with a total backing pressure of 75–90 psig. This gas mixture was expanded through a 50 μm diam nozzle into a vacuum chamber evacuated by a vapor booster pump (Edwards 9B3).

The two-color, optical–optical, double resonance excitation scheme used to prepare NeICl in the ion-pair states is shown schematically in Fig. 2. The 308 nm output of a XeCl excimer laser (Lambda Physik 101) was divided and used to pump two independently tunable dye lasers. The first

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.58.64.71 On: Sat, 30 Nov 2013 17:30:00

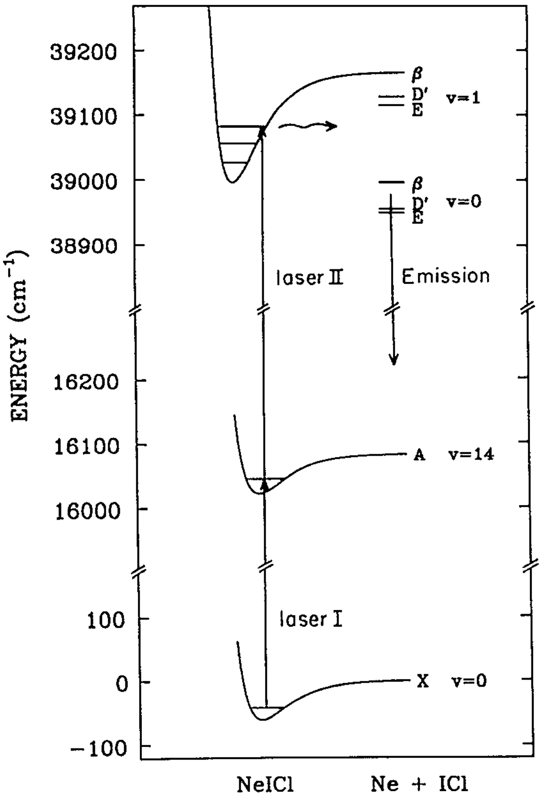

FIG. 2. Schematic potential energy diagram showing a cut of the potential surface along the Ne–ICl dissociation coordinate for the X, A, and ion-pair states. A two-color double resonance excitation scheme is used to prepare NeICl in the ion-pair states with one quantum of ICl stretch. Vibrational predissociation of the complex leaves ICl fragments in the $v = 0$ level of the ICl E, β, and/or D' states, from which emission is detected. Excitation spectra are recorded by scanning laser II, with laser I fixed on the NeICl(14,0)$A \leftarrow X$ transition. Dispersed fluorescence spectra are obtained by changing the wavelength transmitted through the monochromator with lasers I and II fixed on NeICl $A \leftarrow X$ and ion-pair $\leftarrow A$ transitions, respectively.

(Lambda Physik 2002; "laser I"), was operated with Kiton Red 620 dye (Exciton) and was used to selectively promote ground state NeICl to the $v_{\rm ICl} = 14$ or 15 levels of the $A(1)$ electronic state. The second dye laser (a home built model described in detail in Ref. 9; "laser II") was operated with Coumarin 440 or Stilbene 420 dyes (Exciton) and was used to excite $A(1)$ state NeICl to the ion-pair electronic states. The dye laser beams were temporally and spatially overlapped in the vacuum chamber to provide efficient excitation of the transient ($\tau_{\rm vp} = 3$ ns)[18] electronically excited (A state) complexes.

The resulting laser-induced fluorescence originating in the ion-pair electronic states is collected and collimated by a 2 in. diam f/1 lens and focused onto the entrance slit of a 0.25 m, f/4 scanning monochromator with a second 2 in. diam f/4 lens. A blue sensitive photomultiplier tube (Thorn/EMI 9535QA) is mounted directly on the exit slit body to detect emission from the ion-pair states. A red sensitive phototube (Thorn/EMI 9658B) detects the undispersed $A \rightarrow X$ emission imaged by a separate set of f/1 fluorescence collection optics. The resulting emission signals are processed by gated integrators (PAR 162/164) and transferred to a PC/AT-compatible laboratory computer for signal averaging and graphics output. The monochromator and dye laser wavelength drives are equipped with stepping motors for computer-controlled scanning.

III. RESULTS

In our preliminary report, we presented dispersed emission spectra resulting from excitation of uncomplexed ICl to the $v = 0$ and 1 levels of the E, D', and β ion-pair states (see Fig. 1 of Ref. 27). These spectra demonstrated that the dispersed emission patterns resulting from excitation of the lowest lying ion-pair states in ICl provide an unambiguous assignment of the vibrational quantum number of the emitting level. Specifically, the vibrational quantum number is reflected by the shape of the Franck–Condon envelope of the ion pair-to-valence state transitions (no node for $v = 0$, one node for $v = 1$, etc.). Further, the strong propensity for $\Delta\Omega = 0$ radiative transitions between the ion pair and valence states in all of the halogens and interhalogens dictates that the spectra resulting from excitation of single vibrational levels of the E, D', and β states are dominated by $E \rightarrow X$, $D' \rightarrow A'$, and $\beta \rightarrow A$ transitions, respectively.[22] We noted, however, that while emission from the E state was spectrally distinct from that due to the β and D' states, the emission profiles from the latter two states were difficult to distinguish. For example, the Franck–Condon allowed $E \rightarrow X$ transitions occur within the frequency range 24 000–27 500 cm^{-1}, while the strong $\beta \rightarrow A$ and $D' \rightarrow A'$ transitions lie in the frequency interval 23 000–24 000 cm^{-1}. To clarify this issue, we have most recently examined a larger frequency range of the dispersed emission spectra that result from excitation of the low vibrational levels of the ICl β and D' states. As indicated by Fig. 3, we have found that weak continuum features appearing at lower energies than observed previously allow us to distinguish emission due to the D' state from that due to the β state. These features, which appear at various emission frequencies in the spectra from all three ion-pair states, are assigned to bound-free transitions to the multitude of repulsive curves correlating with the ground and low-lying excited states of I + Cl.[28]

A. Excitation of NeICl to $v_{\rm ICl} = 1$

In Fig. 4, we present the fluorescence excitation spectra that result from fixing laser I on the bandhead of the (14,0)$A \leftarrow X$ transition in NeICl while scanning laser II in the vicinity of the (1,14)$\beta \leftarrow A$ transition. In these experiments, the ion pair-to-valence state emission is detected after passing through the 0.25 m monochromator. Because of the large difference in the frequency of emission from the ICl E state as compared to the ICl β and D' states, we are able to use the monochromator as a filter to selectively detect only emission from the E state or only emission from the β and D' states as a function of excitation wavelength. As discussed below, these "selective" excitation spectra prove to be powerful tools in our examination of NeICl in the ion-pair electronic states. To record the spectra shown in both panels of Fig. 4, the monochromator slits are open wide to transmit emission with a bandwidth of ≈700 cm^{-1}. In spectra (a), the monochromator grating is positioned so that only emis-

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.58.64.71 On: Sat, 30 Nov 2013 17:30:00

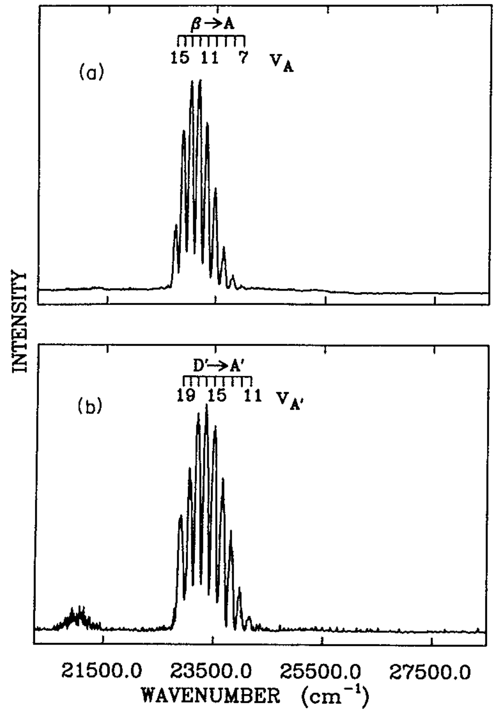

FIG. 3. Dispersed emission spectrum from uncomplexed ICl in the $v = 0$ level of the β and D' ion pair states. Laser I is fixed on the ICl (14,0) $A \leftarrow X$ transition; laser II is positioned on the $(0,14)\beta \leftarrow A$ (22 921 cm^{-1}) transition in (a) and the $(0,14)D' \leftarrow A$ (22 882 cm^{-1}) transition in (b). The dispersed emission patterns on $\beta \rightarrow A$ and $D' \rightarrow A'$ transitions are indistinguishable from one another. Emission from ICl $D'(v = 0)$ can be identified by the weak continuum feature at 21 000 cm^{-1}.

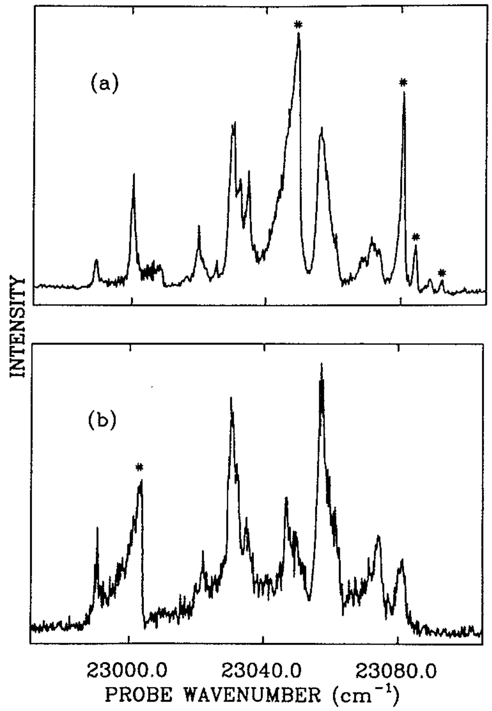

FIG. 4. Fluorescence excitation spectra of NeICl that result from scanning laser II in the vicinity of the ICl $(1,14)\beta \leftarrow A$ transition. Laser I is positioned on the bandhead of the (14,0) $A \leftarrow X$ transition in NeICl. Panel (a) is obtained by selectively detecting emission from the ICl β and/or D' states, while panel (b) is recorded when ICl $E \rightarrow X$ emission is detected. Features marked with an '*' arise from either excitation of A state photofragments resulting from the vibrational predissociation of NeICl $A(v = 14)$ or two photon excitation of ICl.

sion from the ICl β and D' states reaches the photodetector, while in spectrum (b), the monochromator transmits only emission from the ICl E ion-pair state. All of the features shown in Fig. 4(a), with the exception of those marked with an '*' (see below), are due to double resonance excitation of the NeICl complex. A number of NeICl excitation features are observed, corresponding to excitation of a series of van der Waals vibrations (stretching and/or bending) in the ion-pair states. This suggests that excitation of NeICl to the ion-pair states is accompanied by a large change in geometry (bond length and/or angle) relative to the A electronic state.

All of the features assigned to double resonance excitation of NeICl disappear when the identical scan is performed, but with a 100% He/ICl carrier gas mixture. As noted earlier, those peaks marked with an '*' do not arise from double resonance excitation of NeICl. For example, the intense feature at 23 049.0 cm^{-1} (band origin) is due to the $(0,13)\beta \leftarrow A$ transition in uncomplexed ICl. The $v = 13$ level in the A state is populated when NeICl undergoes vibrational predissociation in the A electronic state prior to excitation to the β state. The remaining features at the high energy extreme of the spectrum are assigned to two photon ($\beta \leftarrow X$) excitation of uncomplexed ICl.

As shown in Fig. 4(b), emission is observed from the E state upon excitation of NeICl to van der Waals vibrational levels that also give rise to emission from the β and/or D' states. The E state emission is a direct result of nonadiabatic interactions in the ion-pair states that are absent in uncomplexed ICl. A careful comparison of Figs. 4(a) and 4(b) indicates that both the line positions and relative intensities of the NeICl excitation features are insensitive to the emission channel detected. Thus, the process that gives rise to emission from more than one electronic state is independent of the degree of excitation of the van der Waals stretching and bending coordinates at the $v_{\rm ICl} = 1$ level of excitation.

In Fig. 5, we present the dispersed emission spectrum that results from excitation of the NeICl feature at 23 030.2

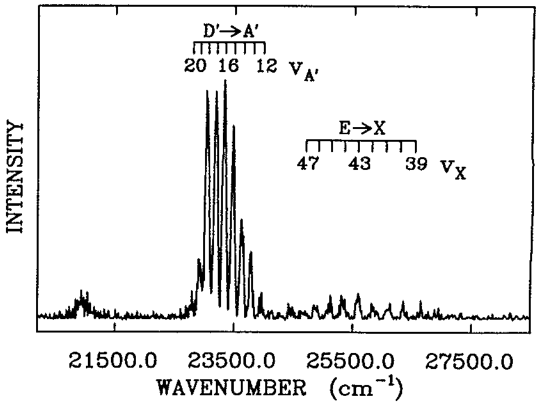

FIG. 5. Dispersed emission spectrum following double resonance excitation of NeICl to the ion pair electronic states with one quantum of ICl stretch. NeICl is excited from the $A(v = 14)$ level by laser II on the valance-to-ion pair state transition at 23 030.2 cm^{-1}.

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.58.64.71 On: Sat, 30 Nov 2013 17:30:00

cm^{-1} [see Fig. 4(a)]. This spectrum, a smooth Franck–Condon envelope with no nodes, is a clear signature of emission from $v = 0$ levels of the ion-pair states. We assume that this emission arises from ICl following vibrational predissociation of the complex. The absence of any emission from NeICl ($v_{\mathrm{ICl}} = 1$) level indicates that vibrational predissociation is rapid compared to the timescale for emission from the ion-pair states ($\tau_{\mathrm{fluor}} \approx 10$ ns).[29] Emission is observed from the ICl E ion-pair state, along with much more intense emission from the β and/or D' state, consistent with the selective excitation spectra [Figs. 4(a) and 4(b)]. On the basis of the continuum features observed in both Fig. 5 and Fig. 3(b) at low energies, we conclude that much of the strong emission observed in the vicinity of 23 500 cm^{-1} must originate from the ICl D' state. Our limited signal-to-noise ratio indicates, however, that a substantial fraction of the observed emission could arise from the β state (see below). We have also recorded the dispersed emission spectrum that results from excitation of the NeICl feature at 23 056.6 cm^{-1} [see Fig. 4(a)]. This spectrum is identical to that shown in Fig. 5, confirming the presence of emission from the E state and demonstrating that substantial emission from the D' state may be a general result.

The calculation of quantitative branching ratios for the nonadiabatic processes that populate the $v = 0$ levels of the ICl E, β and D' ion-pair states following excitation of the $v_{\mathrm{ICl}} = 1$ level requires knowledge of the relative radiative transition moments for the $E \leftrightarrow X$, $\beta \leftrightarrow A$, and $D' \leftrightarrow A'$ transitions.[30] Tellinghuisen and co-workers suggest that the transition moment ratio $D' \leftrightarrow A' / \beta \leftrightarrow A$ is ≈ 2 for ICl;[31] We are unaware of any such estimates of the relative transition moment for the $E \leftrightarrow X$ transition. On the basis of the former result and consideration of the signal-to-noise ratio in our spectra, we believe that as many as 50% of the ICl molecules emitting in the $D' \rightarrow A' / \beta \rightarrow A$ region are in the β state. We are, however, unable to place a lower limit on the contribution to the observed emission from ICl molecules in the β state. Given that the transition moments for the various ion pair-to-valence state transitions in I_2 vary by as much an order of magnitude,[32] we are unprepared to make even tentative estimates of the E state branching ratios observed in our experiments.

B. Excitation of NeICl to $v_{\mathrm{ICl}} = 0$

In contrast to the vibrational predissociation results described above, excitation of NeICl to $v_{\mathrm{ICl}} = 0$ yields a different type of information, since the vibrational predissociation pathway is energetically closed. Thus, the emission observed should arise from the NeICl complex and not ICl photofragments. The fluorescence excitation spectra that result from scanning laser II in the vicinity of the $(0,14)\beta \leftarrow A$ transition is shown in Fig. 6. As in Fig. 4, spectrum (a) was recorded by selectively detecting only emission at frequencies corresponding to the ICl $\beta \rightarrow A$ and/or $D' \rightarrow A'$ transitions (centered at 23 500 cm^{-1}), while spectrum (b) results when only emission in the spectral region of the ICl $E \rightarrow X$ transition (centered at 25 500 cm^{-1}) is monitored. A comparison of the relative line positions demonstrates that the principal features shown in Figs. 4(a) and 6(a) represent transitions to the same set of van der Waals stretching and/or bending levels, but correlating to two different vibrational states of the ICl molecule. For example, the prominent features in the $v_{\mathrm{ICl}} = 1$ region [Fig. 4(a)] at 23 000.5, 23 030.2, and 23 056.6 cm^{-1} are reproduced in the $v_{\mathrm{ICl}} = 0$ region [Fig. 6(a)] at 22 833.0, 22 861.2, and 22 888.1 cm^{-1}. When we record the "selective" excitation spectrum that is sensitive to population with E state electronic character [Fig. 6(b)], however, we find different behavior at $v_{\mathrm{ICl}} = 0$ than that observed at $v_{\mathrm{ICl}} = 1$, [Fig. 4(b)]. For $v_{\mathrm{ICl}} = 0$, excitation of the lower 40 cm^{-1} span of the van der Waals stretching and/or bending energy levels does *not* result in emission with E state character; excitation of the higher energy stretching and/or bending levels *does* result in emission with E state character with a branching ratio that is independent of which van der Waals level is initially populated. The latter observation is reminiscent of the spectra obtained upon excitation of NeICl ($v_{\mathrm{ICl}} = 1$).

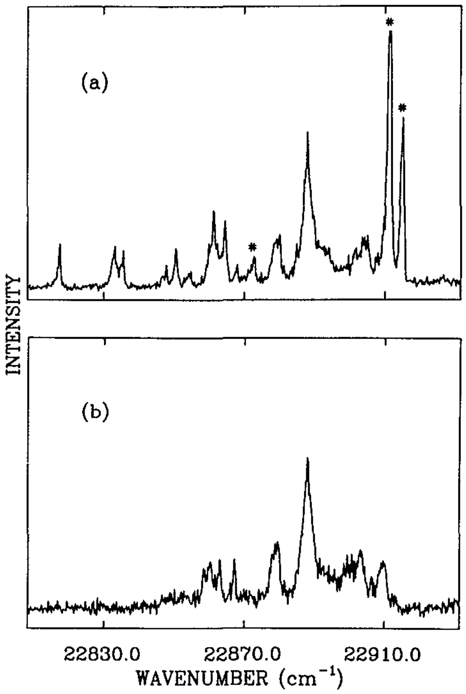

FIG. 6. Fluorescence excitation spectra of NeICl which arise from scanning laser II in the vicinity of the ICl $(0,14)\beta \leftarrow A$ transition. Laser I is positioned on the bandhead of the NeICl $(14,0)A \leftarrow X$ transition. (a) Emission centered at 23 500 cm^{-1} is selectively detected corresponding to the spectral region of ICl $\beta \rightarrow A$ and $D' \rightarrow A'$ transitions. (b) Emission centered at 25 500 cm^{-1} is detected from the spectral region of the ICl $E \rightarrow X$ transition. The "*" indicates two photon transitions of ICl.

In Fig. 7, the dispersed emission spectrum that results from excitation of the NeICl feature at 22 888.1 cm^{-1} [see Fig. 6(a)] is displayed. Emission is observed from NeICl ($v_{\mathrm{ICl}} = 0$) with both E and β / D' state character. This result is consistent with the "selective" excitation spectra discussed above. As in Fig. 5, we find a weak continuum feature at low frequency, indicating that a substantial fraction of the emission at ≈ 23 500 cm^{-1} had D' state character. Based on the analysis described earlier for $v_{\mathrm{ICl}} = 1$, we conclude that up to 50% of the NeICl complexes emitting in this frequency

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP:
130.58.64.71 On: Sat, 30 Nov 2013 17:30:00

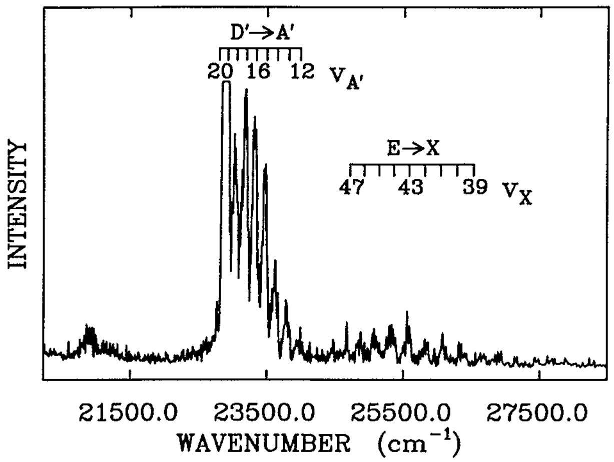

FIG. 7. Dispersed emission spectrum following double resonance excitation of NeICl to the $v_{\mathrm{ICl}} = 0$ level of the ion-pair electronic states. Laser I is fixed on the NeICl $(14,0)A$–X transition; laser II is tuned to excite the NeICl feature at 22 888.1 cm^{-1}.

range have β state character. A similar dispersed emission spectrum, displaying E and D' electronic state character, results from excitation of the NeICl feature at 22 861.2 cm^{-1}. Limitations on the signal-to-noise ratio have made it impossible to record dispersed emission spectra from the van der Waals vibrational levels seen in the lower energy region of the fluorescence excitation spectrum [Fig. 6(a)] that do not appear in the E state "selective" excitation spectrum [Fig. 6(b)]. Thus, we cannot comment on whether the D'/β branching ratio changes for these lower energy stretching and/or bending levels.

C. Excitation of NeICl to $v_{\mathrm{ICl}} = 2$, 3, and 4

We have also examined the behavior of NeICl upon excitation to the $v_{\mathrm{ICl}} = 2$, 3, and 4 vibrational levels to generalize our study of vibrational predissociation dynamics of NeICl in the ion-pair states. Because we observed the same behavior for all of these levels, we present results for $v_{\mathrm{ICl}} = 4$ only. In Fig. 8, the dispersed emission spectrum that results from excitation of a NeICl feature in the vicinity of the $(4,14)\beta \leftarrow A$ transition is presented. In this case, the high energy region (25 500–29 000 cm^{-1}) of the spectrum (not shown) is flat; there is no evidence for emission from the ICl E ion-pair state. The general frequency range of the emission is consistent with the population of either the ICl D' or β states, with the three nodes in the Franck–Condon profile demonstrating that the emission originates in $v = 3$. In Fig. 8(a), we compare the observed emission with that found following excitation of uncomplexed ICl to the $v = 3$ level of the β state. The Franck–Condon profiles of these two emission patterns, while similar, are shifted in frequency relative to one another. In Fig. 8(b), the emission observed following excitation of NeICl is compared with that resulting from excitation of uncomplexed ICl to the $v = 3$ state of the D' state. In this case, the match between the Franck–Condon profiles is exact. Thus, we conclude that the overwhelming majority of the emission ($\geqslant 90\%$) observed is due to the $D' \rightarrow A'$ transition and not the $\beta \rightarrow A$ transition. This Franck–Condon analysis is definitive for the higher ICl ion-pair state vibrational levels ($v \geqslant 3$) since the characteristic emission profiles from the β and D' states differ from one another. This result is fortunate since the bound-free emission patterns are not a reliable signature of the electronic parentage of levels with $v > 2$.

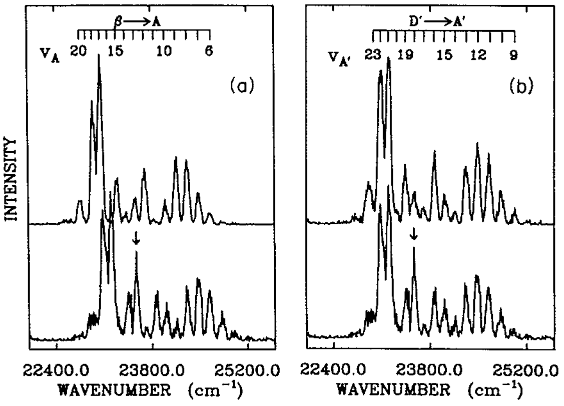

FIG. 8. Dispersed emission spectrum following double resonance excitation of NeICl to ion-pair electronic states with four quanta of ICl stretch. Panel (a) compares the observed emission profile (lower trace) with that found upon excitation of uncomplexed ICl to the $v = 3$ level of the β state (upper trace). Panel (b) shows a similar comparison of the emission resulting from excitation of NeICl (lower trace) with the dispersed emission following excitation of ICl $D'(v = 3)$ (upper trace). NeICl is excited by laser I on the $(14,0)A \leftarrow X$ transition and by laser II at 23 563 cm^{-1}; the resultant laser scatter is marked by an arrow on the lower traces.

Using a combination of Franck–Condon analysis and examination of continuum features, we are able to conclude that the emission that results from excitation of NeICl to the $v_{\mathrm{ICl}} = 3$ level predominately originates in the $v = 2$ level of the ICl D' state. No emission from the E state is observed. Similarly, when NeICl is excited to the $v_{\mathrm{ICl}} = 2$ level, no emission is observed from the E state. Emission that is characteristic of the $v = 1$ level of the ICl β and/or D' states is observed. As at $v_{\mathrm{ICl}} = 0$ and 1, the emission profile confirms the importance of emission from the D' state and is consistent with a substantial β state component.

In summary, we have observed emission characteristic of multiple ion-pair electronic states following excitation of the NeICl van der Waals complex. The relative contributions of emission from the E, β, and D' states to the overall emission signal is sensitive to the degree of excitation of the I–Cl vibrational coordinate (i.e., the value of v_{ICl}). With the exception of complexes excited to $v_{\mathrm{ICl}} = 0$, the emission patterns observed are independent of the degree of excitation of the van der Waals stretching/bending degree of freedom. Finally, for $v_{\mathrm{ICl}} \geqslant 1$, rapid vibrational predissociation of the complex occurs, following a $\Delta v_{\mathrm{ICl}} = -1$ propensity rule.

IV. DISCUSSION

A. Initial state preparation

Optical–optical double resonance excitation has been used to prepare NeICl vdW complexes in ion-pair electronic states through NeICl intermediate levels which correlate with the A(1) valence electronic state of ICl. The strong

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.58.64.71 On: Sat, 30 Nov 2013 17:30:00

propensity for $\Delta\Omega = 0$ on ICl valence to ion-pair state transitions[22] suggests that the observed transitions in NeICl gain their electronic oscillator strength from the ICl $\beta(1) \leftarrow A(1)$ transition. The presence of the Ne atom may induce nonadiabatic couplings between the NeICl levels correlating with the closely spaced $\beta(1)$, $D'(2)$, and $E(0^+)$ ion-pair states of ICl, which do not occur in uncomplexed ICl. Thus, the initially prepared NeICl levels may have mixed electronic character derived from all three of these ion-pair states. In order to evaluate the electronic character of the initially prepared NeICl vdW levels, we have examined dispersed fluorescence spectra obtained when NeICl is prepared in the ion-pair states with zero quanta of ICl vibrational excitation ($v_{\rm ICl} = 0$). Following excitation of NeICl($v_{\rm ICl} = 0$), the emission should arise from the NeICl complex itself, and not from ICl, since the vibrational predissociation decay channel is energetically closed. Thus, we may use the dispersed emission spectra to determine the electronic character of the levels prepared by optical–optical double resonance excitation. The NeICl ($v_{\rm ICl} = 0$) emission should be free from the influence of dynamical processes which may be present for NeICl ($v_{\rm ICl} \geqslant 1$).

The dispersed emission spectrum resulting from excitation of the NeICl ($v_{\rm ICl} = 0$) feature at 22 888.1 cm^{-1} (Fig. 7) has components in the regions of the ICl $D'(2) \rightarrow A'(2)$, $E(0^+) \rightarrow X(0^+)$, and $\beta(1) \rightarrow A(1)$ transitions. This indicates that the electronic character of the initially prepared level is derived from all three of the ICl ion-pair states. Selective excitation spectra have shown that the electronic character of NeICl ($v_{\rm ICl} = 0$) changes with the initial vdW vibrational level selected. NeICl features appearing in the lowest 40 cm^{-1} of the excitation spectrum do not exhibit E state emission and therefore lack ICl E state character.

The initially prepared NeICl ($v_{\rm ICl} = 0$) levels can be described within the framework of an exact molecular eigenstate picture.[33] Each exact NeICl eigenstate is composed of a single zero-order vdW level with ICl $\beta(1)$ character and a group of zero-order vdW levels with ICl $D'(2)$ or $E(0^+)$ character which are strongly coupled to the β level. The β state component provides the oscillator strength for the electronic transition from the A state to the ion-pair state in NeICl. The number of $D'(2)$ and $E(0^+)$ levels coupled to the β level depends on the energy range of the nonadiabatic couplings, $W_{\beta D}$, and $W_{\beta E}$, and the density of vdW levels correlating with ICl D' and E states, $\rho_{D'}$ and ρ_E, within these energy ranges. The vdW levels with ICl D' and E zero-order character are radiatively coupled to NeICl levels in the A' and X states, respectively. In the exact molecular eigenstate model, the wave function for the initially prepared NeICl ($v_{\rm ICl} = 0$) level in the ion-pair state may be expressed as

$$\Psi = d\psi_{D'} + e\psi_E + b\psi_\beta,$$

where d, e, and b represent the amount of ICl D', E, and β electronic character in the NeICl ion-pair state wave function.

The dispersed emission spectrum reflects the transition dipole matrix elements between the NeICl ion-pair state and NeICl in final states correlating with ICl in the $A'(2)$, $A(1)$, and $X(0^+)$ states. If we assume that the $A'(2)$, $A(1)$, and $X(0^+)$ valence electronic states have nonzero dipole matrix elements with only the $D'(2)$, $\beta(1)$, and $E(0^+)$ components of the NeICl ($v_{\rm ICl} = 0$) ion-pair state, respectively, then the NeICl ($v_{\rm ICl} = 0$) dispersed fluorescence spectrum reveals the "$D'(2)$", "$\beta(1)$", and "$E(0^+)$" character of the initial state. The squares of the coefficients d, b, and e can be obtained from the intensities of the three types of emissions when the relative electronic transition strengths are known. From the relative intensities of the $D' \rightarrow A'$ and $\beta \rightarrow A$ emissions, we estimate that the D' contribution to the NeICl ion-pair state wave function is at least equal to that from the ICl β state, i.e., $d/b \geqslant 1$. A similar comparison is not possible for the E state since the transition strength of $E \rightarrow X$ relative to $\beta \rightarrow A$ or $D' \rightarrow A'$ is not known.

B. Energetics

The positions of the NeICl vdW levels with respect to the E, D' and β state asymptotes of ICl can be determined from fluorescence excitation spectra. The calculation requires evaluating the spectral shifts of the NeICl excitation features from the corresponding ICl transition frequencies and knowing the binding energy of NeICl in a valence electronic state. For example, the shifts of the NeICl excitation features observed in the region of the ICl $\beta \leftarrow A(0,14)$ are obtained by comparing the line positions observed in the spectrum with the known transition energy for ICl $\beta \leftarrow A(0,14)$. Most of the NeICl excitation features are shifted to lower energy of the ICl transition, demonstrating that the vdW levels in the ion-pair state are more deeply bound than in the valence state. This spectral shift would then be combined with an estimate of the NeICl binding energy in the $A(v = 14)$ state to determine the energies of the NeICl ion-pair state vdW levels. The binding energy of Ne to ICl $A(v = 14)$ was estimated by Drobits and Lester to be 44 cm^{-1}.[9] For the reasons discussed in the Appendix, we have assumed a value of 60 cm^{-1} for the NeICl binding energy in the $A(v = 14)$ state in the present work. The positions of the optically accessed NeICl ($v_{\rm ICl} = 0$) vdW levels in the ion-pair states relative to the ICl($v = 0$)$\beta(1)$, $D'(2)$, and $E(0^+)$ asymptotes are shown on a schematic potential energy diagram in Fig. 9. We find that of all the NeICl vdW features experimentally observed lie below the E state asymptote for $v_{\rm ICl} = 0$. The same cutoff is observed for NeICl with $v_{\rm ICl} = 1$–4 (with the assumed binding energy).

A closer examination of Fig. 9 reveals three distinct energy regimes in the NeICl ($v_{\rm ICl} = 0$) vdW vibrational manifold. In the highest energy regime (Region III), between the ICl β and E state dissociation limits, no NeICl features are detected. At intermediate energies (Region II), below the ICl E state asymptote and above approximately 22 860 cm^{-1}, the experimentally observed NeICl vdW levels have D', E, and β electronic character. The lowest NeICl vdW levels (Region I), appearing below 22 860 cm^{-1}, lack an observable E state component and have D'/β electronic character. We propose a physically intuitive model to explain these three regimes below.

Region III. Since the propensity rules operative for the double resonance excitation scheme ($\Delta\Omega = 0$ on valence to ion-pair state transitions) suggest that the NeICl ($v_{\rm ICl} = 0$)

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP:

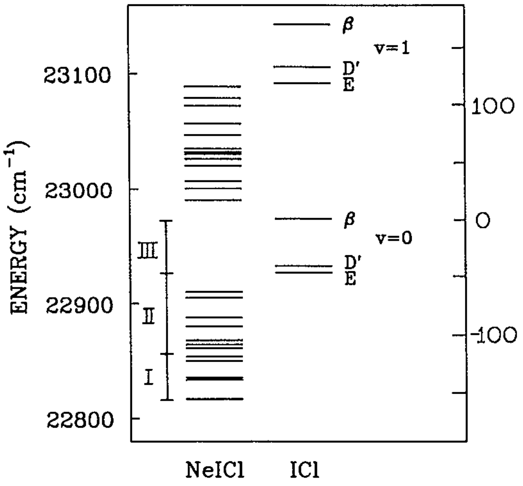

FIG. 9. Potential energy level diagram showing positions of experimentally observed NeICl vdW vibrational levels relative to the $v = 0$ and 1 levels of the ICl ion-pair states. Vertical scales are energies relative to NeICl $A(v = 14)$ (left side) and ICl $\beta(v = 0)$ asymptote (right side). Regions I, II, and III are defined in the text. The binding energy (D_0) of Ne to ICl $A(v = 14)$ is assumed to be 60 cm^{-1}.

eigenstates should be prepared with some β state character, we might have expected to observed vdW vibrational levels all the way up to the ICl β state dissociation limit. These levels are not experimentally observed, however, possibly due to a rapid nonradiative decay process which prevents their detection. Above the dissociation limit correlating with ICl $E(v = 0)$ + Ne, there will be a continuum of levels superimposed on the discrete levels of the vdW potentials correlating with ICl $\beta(v = 0)$ + Ne in a zero-order description. If nonadiabatic coupling occurs between the discrete levels and the continuum of ICl $E(v = 0)$ + Ne, the NeICl complex may undergo electronic predissociation. Thus, the NeICl vdW levels above the ICl E state dissociation limit may have only a limited lifetime. Transitions terminating on these levels will be homogeneously broadened, to the point that excitation features accessing these levels may be indistinguishable from background. The onset of the homogeneously broadening would be sharp, starting with the first NeICl vibrational level lying above the E state dissociation limit, consistent with our observations. Based on this explanation and the signal-to-noise ratio in our excitation spectra, we estimate that the levels above the E state dissociation limit have a lifetime of $\leqslant 1$ picosecond. A possible alternative explanation for the lack of NeICl levels above the ICl $E(v = 0)$ asymptote is poor Franck–Condon overlap with NeICl $A(v = 14)$.

Region II. NeICl levels in this region have electronic character derived from the ICl D', E, and β states. This suggests that the Ne atom induces strong nonadiabatic couplings between all three of these ICl electronic states. Selective excitation spectra (Fig. 6), obtained while monitoring emission with E or D'/β character only, exhibit similar relative intensity patterns in this energy regime. This indicates that the E state component of the NeICl wave function (e) is the same for all vdW levels in Region II.

The linewidths of the features in the fluorescence excitation spectrum are on the order of 1 cm^{-1}, which is significantly greater than the bandwidths of lasers I and II. The breadth of the excitation features may reflect the energy range of the nonadiabatic couplings, $W_{\beta D'}$, and $W_{\beta E}$. If this is the case, the linewidth of the excitation features would be a measure of the strength of the nonadiabatic couplings and the number of vdW levels with ICl D' and E zero-order character within this energy range. The excitation spectrum would follow the pattern of NeICl eigenstates having an ICl β electronic component. Alternatively, the linewidth may be due to rotational structure with contributions from the rotational distribution prepared in the A state by laser I and the rotational transitions pumped by laser II on the $\beta \leftarrow A$ transition. Our trial rotational band contour simulations suggest that this conjecture is unlikely for a molecule as heavy as NeICl, particularly in light of the small number of A state rotational levels populated by laser I. Finally, the linewidth of the excitation features could arise from homogeneous lifetime broadening, but this is unlikely since we do not expect any dynamical processes to occur for NeICl ($v_{\rm ICl} = 0$) in this region.

Region I. E state emission is not detected following excitation of NeICl ($v_{\rm ICl} = 0$) to vdW levels in this energy regime. From this observation we conclude that these NeICl levels have no ICl E state component to their electronic wave functions, i.e., the coefficient e is approximately zero for NeICl ($v_{\rm ICl} = 0$) vdW levels below 22 860 cm^{-1}. The NeICl eigenstates would lack E state character if the β–E coupling was weak, $W_{\beta E} \approx 0$, or if the number of vdW levels correlating with the ICl E state was sufficiently small. If the zero-order vdW well correlating with E is shallow compared to the zero-order β and D' wells in the spectroscopically accessed region of the intermolecular potential, there may simply be no bound vdW levels with zero-order E state character. Alternatively, the sudden onset of E state emission above Region I could suggest an abrupt change in the overlap of the zero-order potentials, for example, an electronic curve crossing between the vdW potentials correlating with the ICl β and E states. NeICl levels located above the curve crossing would have mixed electronic character, while levels occurring below the curve crossing would not be coupled ($W_{\beta E} = 0$).

C. Vibrational predissociation dynamics

The dispersed fluorescence measurements indicate that NeICl complexes prepared in the ion-pair state with one or more quanta of ICl vibrational excitation rapidly undergo vibrational predissociation ($\tau_{\rm vp} < 10$ ns). Fluorescence is detected from ICl photofragments which are left in the β, D', or E ion-pair states and contain one less quantum of ICl vibrational excitation. A $\Delta v = -1$ propensity rule for vibrational predissociation appears to be obeyed for NeICl in the ion-pair states, as found previously for halogen–rare gas complexes in valence electronic states.[1] Thus, one quantum of ICl vibrational excitation must be sufficient to break the NeICl vdW bond, which places an upper limit on the NeICl bond dissociation energy in the ion-pair state (see Appendix).

The fluorescence excitation spectra for NeICl prepared

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.58.64.71 On: Sat, 30 Nov 2013 17:30:00

with 1–4 quanta of ICl stretch in the ion-pair states ($v_{\mathrm{ICl}} = 1$–4) have a remarkably similar appearance to one another and to the excitation spectrum obtained for NeICl ($v_{\mathrm{ICl}} = 0$), when selectively detecting emission from the β/D' states. All exhibit a similar series of NeICl vdW excitation features, corresponding to excited bending and/or stretching levels in the ion-pair state. The vdW features extend over a $> 100\ \mathrm{cm}^{-1}$ energy range and terminate (at the low energy extreme) before reaching the ICl asymptotes for the next lower vibrational level. The energy spacings between corresponding NeICl features in the excitation spectra are nearly unchanged with ICl vibrational excitation. (The relative positions of the ICl A state photofragment peak and accidental ICl double resonance peaks, however, move with respect to the NeICl vdW features.) The similarity of the fluorescence excitation profiles with v_{ICl} indicates that same set of vdW vibrational levels are accessed in NeICl potentials correlating to different ICl vibrational levels.

The relative energies of the ICl β, D', and E states change with ICl vibrational excitation, thereby changing the positions of the NeICl ion-pair state asymptotes. For example, the spacing between the ICl β and E states increases from 50.7 to 54.7 cm^{-1}, while the spacing between the ICl β and D' states decreases from 37.1 to 34.1 cm^{-1} between $v = 1$ and 2.[22] (The spacing between sequential vibrational levels within the same ion-pair electronic state decreases much more slowly, from 169.4 to 166.6 cm^{-1} upon going from $v = 0$ to 4 of the β state.) Though this suggests that the zero-order NeICl vdW levels that correlate with the ICl D' and E states may shift relative to the zero-order β states upon ICl vibrational excitation, our experimental spectra demonstrate that *the pattern of the observed NeICl eigenstates is only slightly affected.* We therefore assume in the discussion that follows, that the electronic character of the initially prepared NeICl vdW levels is not changed by vibrational excitational of the ICl stretch. The NeICl eigenstates in $v_{\mathrm{ICl}} = 1$–4 are taken to be of the same mixed electronic character as found for NeICl ($v_{\mathrm{ICl}} = 0$) through dispersed fluorescence measurements; vdW levels in the higher energy region of the progression (Region II) have ICl D', E, and β character, while the lower energy levels (Region I) are assumed to lack the E state component.

The dispersed fluorescence results reveal the electronic character of the ICl photofragments following vibrational predissociation ($\Delta v = -1$) of the NeICl complex. For NeICl prepared with $v_{\mathrm{ICl}} = 2$–4, the ICl fragments are predominately left in the D' electronic state. For NeICl ($v_{\mathrm{ICl}} = 1$), emission is detected from ICl products in both the D' and E states. Again, we note that some of the emission in the D' region could arise from the β state. This does not imply, however, that the electronic character of the ICl fragments is the same as that of the initially excited NeICl. The ICl E state product channel closes above $v_{\mathrm{ICl}} = 1$ and a strong preference for the ICl D' state product channel is observed for $v_{\mathrm{ICl}} > 2$. A comparison of the electronic state(s) populated in the ICl fragments with the mixed electronic character of the initially prepared NeICl eigenstates points to the selectively of the nondiabatic interaction in the vibrational predissociation process. Furthermore, the vdW vibrational level dependence of the NeICl eigenstate prepared is lost during vibrational predissociation of the complex. Therefore, from the different behavior of the NeICl complex prepared with $v_{\mathrm{ICl}} = 0$ and 1, we conclude that vibrational predissociation of the vdW complex is accompanied by nonadiabatic electronic state changing processes.

The vibrational predissociation dynamics of a vdW complex taking place on a single adiabatic potential energy surface is well understood. A quantum of energy initially localized in the diatom vibration is transferred into the weak vdW bond, causing it to rupture. The rate of vibrational predissociation and the internal state distribution of the fragments can be evaluated by considering the coupling between the initially prepared bound state of the complex and the continuum of levels corresponding to the separated fragments. A simple correlation has been derived that relates the rate of vibrational predissociation to the "momentum gap," ($2\mu\Delta E_{\mathrm{vib}}$), where μ is the reduced mass of the complex and ΔE_{vib} is the amount of energy released from vibration.[34] In this model, the rate of vibrational predissociation is directly dependent on the overlap between the bound state van der Waals vibrational wave function and the highly oscillatory continuum wave function of the separating fragments. The van der Waals potential energy curves correlating to the initial and final diatom vibrational levels are assumed to be identical, though displaced in energy by ΔE_{vib}. The degree of oscillation of the continuum wave function is related to the total translational energy of the separating fragments. Thus, the magnitude of the overlap, and the rate of vibrational predissociation, is determined by the translational energy release. When several final states are considered, the momentum gap strongly favors exit channels that minimize energy released to translational degrees of freedom. The strength of the vibrational coupling has also been shown to influence the vibrational predissociation dynamics.[10]

A generalized theoretical framework has not been developed to describe vibrational predissociation dynamics involving more than one electronic potential energy surface. Certainly, nonadiabatic couplings increase the number of possible dissociation channels. From the momentum gap law, we might again expect a preference for those exit channels that minimize the energy released into translational motion of the fragments.[34] For NeICl, the momentum gap rationale suggests that the ICl β state should be preferentially populated upon vibrational predissociation of the complex, rather than the D' and E states as experimentally observed. The bound-continuum matrix elements are determined by the oscillatory cancellation of the bound and continuum wave functions, which could easily be affected by the small changes between the ICl β, D', and E potentials. We anticipate that the shapes of the five zero-order van der Waals potentials correlating with Ne + ICl β, D', and E will differ from one another, as previously observed in the van der Waals potential curves of a rare gas atom with an open-shell atom in different spin–orbit states.[23,24] This suggests that the continuum wave functions originating from the five different zero-order potentials, with one less quantum of ICl vibrational excitation, may have different overlaps with the initial

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.58.64.71 On: Sat, 30 Nov 2013 17:30:00

bound state wave function. The oscillatory form for each of the continuum wave functions is determined by the steepness and position of the repulsive wall in addition to its energy above the asymptote (dissociation limit) of the vdW potential. It is plausible that the continuum wave function associated with a zero-order D' potential may be less oscillatory in the region of the initially prepared bound state than the continuum wave functions derived from the zero-order β or E state potentials. This would result in a more favorable overlap with the bound state wave function and a preferential population of the ICl D' state. An alternative view is that the observed selectivity for one of the three ICl ion-pair states arises from the relative strength of the nonadiabatic couplings between the initial NeICl bound state (with mixed ICl electronic parentage) and the final states correlating with Ne + ICl β, D', and E. In this case, the final selectivity does not arise solely from considerations of the rovibrational dynamics of the complex, but explicitly involves the impact of the recoiling rare gas atom on the interaction between ICl electronic state wave functions. The momentum gap argument advanced above does not consider the relative strength of these nonadiabatic couplings, which we postulate may be an additional factor involved in the preferential population of the ICl D' state.

ACKNOWLEDGMENTS

This research was sponsored by the National Science Foundation through the Physical Chemistry Program. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. M.I.L. thanks the Dreyfus Foundation for a Teacher–Scholar Award. T.A.S. thanks Swarthmore College for a Eugene M. Lang Faculty Fellowship and the Department of Chemistry of the University of Pennsylvania for its hospitality during his sabbatical leave (1988–89).

APPENDIX: ESTIMATION OF NeICl BINDING ENERGIES

Previously, Drobits and Lester estimated the binding energies of Ne to ICl in the X, A, and ion-pair states.[9] In the earlier work, as in the present experiments, the NeICl complex was promoted to the ion-pair states by optical–optical double resonance excitation. The use of cut-off filters in the earlier experiments restricted the detected emission to $E \rightarrow X$ fluorescence ($\nu > 25\,000$ cm^{-1}) and, consequently, the excitation spectrum was attributed to $E(v=1) \leftarrow A(v=14) \leftarrow X(v=0)$ transitions in NeICl. The dominant features of the NeICl excitation spectrum were assigned to a progression in the vdW stretching mode in the ion-pair state. A one-dimensional Birge–Sponer analysis of the vdW stretching mode was used to evaluate the binding energy of Ne to ICl $E(v=1)$ as 88 cm^{-1}. The bond dissociation energies for NeICl in the A and X states were then determined from the spectral shifts of the vdW features relative to uncomplexed ICl on $E \leftarrow A$ and $A \leftarrow X$ transitions, yielding $D_0(v_A = 14) = 44$ cm^{-1} and $D_0(v_X = 0) = 48$ cm^{-1}.[9]

The present results and analysis differ from the earlier work in two important ways. The biggest change comes about from referencing the vdW vibrational levels in the ion-pair state to the ICl β state asymptote, rather than the ICl E state asymptote. This increases the estimated binding energy of Ne to ICl($v=1$) in the ion-pair state by 50.7 cm^{-1}.[22] The estimated binding energies for NeICl in the A and X state will not be affected by this change. Further, the improved detection sensitivity, afforded by collecting emission in the β/D' fluorescence region, permitted observation of additional features in the NeICl excitation spectra, causing us to question the previous one-dimensional analysis. We have therefore chosen to rely on other measurements to determine the NeICl binding energies.

In the present experiments, we have found that one quantum of ICl vibration in the ion-pair state is sufficient to dissociate NeICl in the $v_{\mathrm{ICl}} = 1$–4 levels of the ion-pair state. The energy released upon $v=1 \rightarrow v=0$ relaxation in the ICl β state is 169.4 cm^{-1},[22] which must be an upper limit for the binding energy for NeICl in the ion-pair state. This combined with the spectral shift of the lowest energy vdW feature relative to the ICl $\beta \leftarrow A$ transition energy (89.1 cm^{-1}) places an upper limit on the binding energy of Ne to ICl $A(v=14)$ at <80 cm^{-1}. We also know that the binding energy of NeICl in the ion-pair state must be $\geqslant 100$ cm^{-1}, since we observe features in the excitation spectra (see Figs. 4 and 6) over this range of energies.

Previous experiments on the photofragmentation dynamics of NeICl complexes in the A state can be used to refine the upper limit of the Ne–ICl bond energy in the A state. Drobits and Lester observed extensive rotational excitation of the ICl A state fragments following vibrational predissociation of NeICl.[7] Following a suggestion by Janda,[35] if we assume that the observed product rotational distribution extends to the highest J allowed by conservation of energy, an upper limit for the binding energy is obtained. The rotational product distribution following vibrational predissociation of NeICl A state $v=23$ level extends to $J=12$, consistent with a NeICl bond energy of $\leqslant 57$ cm^{-1}. A comparison of the spectral shifts for NeICl on $A \leftarrow X$ transitions suggests that the binding energy of Ne to ICl($v=14$) should be $\leqslant 60$ cm^{-1}. We adopt the upper limit value, 60 cm^{-1}, for our present work. This also implies an upper limit for the binding energy in the ion-pair states of 150 cm^{-1}.

[1] D. H. Levy, Adv. Chem. Phys. **47**, 323 (1981).

[2] K. C. Janda, Adv. Chem. Phys. **60**, 201 (1985).

[3] D. D. Evard, C. R. Bieler, J. I. Cline, N. Sivakumar, and K. C. Janda, J. Chem. Phys. **89**, 2829 (1988), and references therein.

[4] J. I. Cline, B. P. Reid, D. D. Evard, N. Sivakumar, N. Halberstadt, and K. C. Janda, J. Chem. Phys. **89**, 3535 (1988).

[5] N. Sivakumar, J. I. Cline, C. R. Bieler, and K. C. Janda, Chem. Phys. Lett. **147**, 561 (1988), and references therein.

[6] J. I. Cline, N. Sivakumar, D. D. Evard, C. R. Bieler, B. P. Reid, N. Halberstadt, S. R. Hair, and K. C. Janda, J. Chem. Phys. **90**, 2605 (1989).

[7] J. C. Drobits and M. I. Lester, J. Chem. Phys. **89**, 4716 (1988), and references therein.

[8] R. L. Waterland, J. M. Skene, and M. I. Lester, J. Chem. Phys. **89**, 7277 (1988), and references therein.

[9] J. C. Drobits and M. I. Lester, J. Chem. Phys. **86**, 1662 (1987).

[10] R. L. Waterland, M. I. Lester, and N. Halberstadt, J. Chem. Phys. **92**, 4261 (1990).

[11] O. Roncero, J. A. Beswick, N. Halberstadt, P. Villarreal, and G. Delgado-Barrio, J. Chem. Phys. **92**, 3348 (1990).

[12] G. Kubiak, P. S. H. Fitch, L. Wharton, and D. H. Levy, J. Chem. Phys.

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.58.64.71 On: Sat, 30 Nov 2013 17:30:00

68, 4477 (1978).

[13] N. Goldstein, T. L. Brack, and G. H. Atkinson, J. Chem. Phys. **85**, 2684 (1986).

[14] T. A. Stephenson, W. R. Simpson, J. R. Wright, H. P. Schneider, J. W. Miller, and K. E. Schultz, J. Phys. Chem. **93**, 2310 (1989).

[15] J. A. Beswick, R. Monot, J.-M. Phillippoz, and H. van den Bergh, J. Chem. Phys. **86**, 3965 (1987).

[16] C. Jouvet and B. Soep, J. Chem. Phys. **80**, 2229 (1984).

[17] C. Jouvet and J. A. Beswick, J. Chem. Phys. **86**, 5500 (1987).

[18] J. C. Drobits, J. M. Skene, and M. I. Lester, J. Chem. Phys. **84**, 2896 (1986).

[19] J. C. D. Brand and A. R. Hoy, J. Mol. Spectrosc. **114**, 197 (1985).

[20] J. A. Coxon and M. A. Wickramaaratchi, J. Mol. Spectrosc. **79**, 380 (1980).

[21] J. C. D. Brand, D. Bussières, and A. R. Hoy, J. Mol. Spectrosc. **113**, 388 (1985).

[22] D. Bussières and A. R. Hoy, Can. J. Phys. **62**, 1941 (1984).

[23] V. Aquilanti, R. Candori, and F. Pirani, J. Chem. Phys. **89**, 6157 (1988).

[24] C. Dedonder-Lardeux, C. Jouvet, M. Richard-Viard, and D. Solgadi, J. Chem. Phys. **92**, 2828 (1990).

[25] K. Yamanouchi, S. Isogai, M. Okunishi, and S. Tsuchiya, J. Chem. Phys. **88**, 205 (1988).

[26] V. Aquilanti, G. Liuti, F. Pirani, and F. Vecchiocattivi, J. Chem. Soc. Faraday Trans. 2 **85**, 955 (1989).

[27] T. A. Stephenson, Y. Hong, and M. I. Lester, Chem. Phys. Lett. **159**, 549 (1989).

[28] J. C. D. Brand and A. R. Hoy, J. Mol. Spectrosc. **114**, 219 (1985).

[29] J. G. Eden, M. L. Dlabal, and S. B. Hutchison, IEEE J. Quantum Electron. **17**, 1085 (1981).

[30] In our experiments, we measure the total integrated emission intensity at a particular wavelength. These intensities are not simply related to the relative populations in the ICl ion-pair states due to the presence of alternative modes for radiative relaxation of the ion-pair states. For example, we know that emission from the ICl D' state occurs on bound-free transitions to repulsive curves correlating with I + Cl in addition to the $D' \rightarrow A'$ transition monitored in the dispersed emission experiment. The relative fraction of emission on the transition monitored, which is not presently known, would be needed to correlate the integrated intensity to the ICl ion-pair state branching ratio.

[31] J. D. Spivey, J. G. Ashmore, and J. Tellinghuisen, Chem. Phys. Lett. **109**, 456 (1984).

[32] J. Tellinghuisen, Chem. Phys. Lett. **99**, 373 (1983).

[33] K. F. Freed and A. Nitzan, J. Chem. Phys. **73**, 4765 (1980).

[34] J. A. Beswick and J. Jortner, Adv. Chem. Phys. **47**, 363 (1981); G. E. Ewing, J. Phys. Chem. **91**, 4662 (1987); R. J. Le Roy, M. R. Davies, and M. E. Lam, J. Phys. Chem. (in press).

[35] K. C. Janda and C. R. Bieler, in *Atomic and Molecular Clusters*, edited by E. R. Bernstein (Elsevier, Amsterdam, 1990), p. 455.

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: