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$\Phi = 3$. [This is too extreme an assumption, since it implies a slightly negative rate constant for $k(v' = 1 | v = 1)$.] Assuming, alternatively, that the increase in $v' = 2$ is entirely due to $F + HCl(v = 1)$, $(\bar{V}')_{v=1} = 26.0 \text{ kcal mole}^{-1}$ and $\Phi = 9$. Experiments now in progress give a figure for Φ at the lower end of this range: $\Phi = 3-4$.

¹²R. N. Coletharp, S. D. Worley, and A. E. Potter, *J. Appl. Opt.* **10**, 1786 (1971).

¹³G. Hancock, C. Morley, and I. W. M. Smith, *Chem. Phys. Letters* **12**, 193 (1971), found qualitative evidence for (ii) in the system $O + CS \rightarrow CO + S$.

¹⁴D. L. Thompson, *J. Chem. Phys.* **56**, 3570 (1972).

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Raman Spectrum of Pyrazine Crystal Excited by the Light of the Absorption Edge

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In a previous paper,¹ we reported that the fluorescence spectrum of pyrazine vapor exhibits a long progression in the hydrogen bending vibration $\nu_5(b_{2g})$ of 920 cm^{-1} and that the Raman intensity of the same vibration shows a remarkable preresonance effect in the excitation wavelength region from 6328 to 4047 Å. Since appearance of the nontotally symmetric vibration ν_5 in the fluorescence spectrum implies vibronic coupling through this vibration between the lowest electronic excited state (${}^1B_{3u}, n-\pi^*$) and some higher excited states, the results obtained were regarded as the first example supporting the vibronic theory of Raman intensities developed by Albrecht.³

In the present Communication, we report a more impressive preresonance Raman effect, which was obtained with the exciting light very close to the long wavelength edge of the electronic absorption. The 0-0 band of the longest wavelength absorption of pyrazine crystal is located at about 3330 Å. Therefore 3371 Å light of the N_2 laser is very close to the 0-0 band and it may be used as an exciting light for the Raman spectrum. However, at room temperature or even at 77°K, the 3371 Å excitation induces strong fluorescence because of a broad absorption due to hot bands extending beyond 3371 Å and it interferes with observation of the Raman spectrum. In order to avoid the electronic excitation due to the hot bands, the temperature of the crystal was decreased to 4.2°K and we succeeded in obtaining the Raman spectrum with no trace of fluorescence. Figure 1 shows the Raman spectrum thus obtained.⁴ For comparison, the spectrum of the same sample excited by 5145 Å Ar^+ laser is also shown in the figure.

As is seen from the figure, the Raman line ν_5 at 920 cm^{-1} is extremely weak in the spectrum of 5145 Å excitation, but it becomes the most intense Raman line with 3371 Å excitation. Similar but less pronounced intensity enhancement is seen also for the Raman lines ν_{6a} and ν_{10a} . If we take the Raman line ν_4 as an internal intensity standard, the intensity of the ν_5 line of the 3371 Å excitation amounts to as large as 140 times the intensity of the same line of the 5145 Å excitation. In the 3371 Å excitation, we

observed also the overtone of ν_5 whose intensity was about 1/6 of that of the fundamental.

The impressive preresonance effect described above provides us additional conclusive evidence supporting the theoretical prediction by Albrecht that the vibration responsible for the vibronic coupling between the two electronic excited states exhibits a particularly large preresonance Raman effect. Appearance of the overtone line suggests that the spectrum of 3371 Å excita-

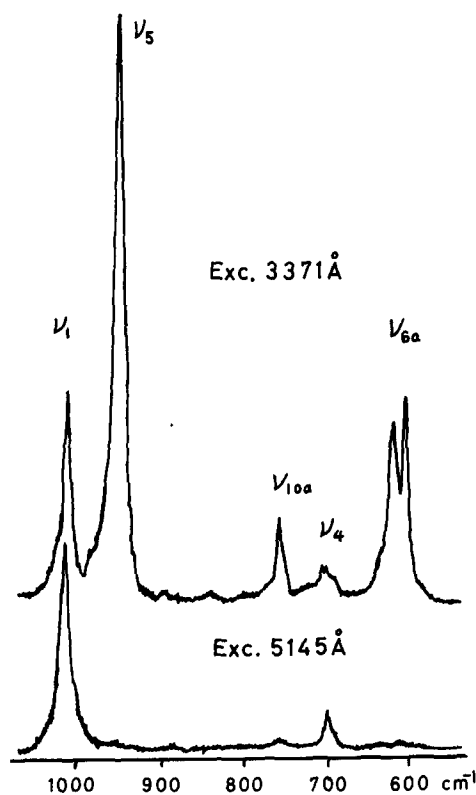


FIG. 1. Raman spectrum of pyrazine crystal excited by the 3371 Å line of N_2 laser at 4.2°K (top) and by the 5145 Å line of Ar^+ laser at 77°K (bottom). The $\nu_5(920 \text{ cm}^{-1})$ band is at 950 cm^{-1} in the crystal. The fine structure of the ν_{6a} band may be due to Davydov splitting. $\nu_4(b_{2g}) = 700 \text{ cm}^{-1}$, $\nu_{10a}(b_{1g}) = 750 \text{ cm}^{-1}$, $\nu_1(a_g) = 1015 \text{ cm}^{-1}$.

tion represents an intermediate stage from a pre-resonance Raman effect to a rigorous one.

¹ M. Ito, I. Suzuka, Y. Udagawa, N. Mikami, and K. Kaya, *Chem. Phys. Letters* (to be published).

² The vibrational mode numbers and the choice of the symmetry

axes are the same as those used in K. K. Innes, J. P. Byrne, and I. G. Ross, *J. Mol. Spectry*, **22**, 125 (1967).

³ A. C. Albrecht, *J. Chem. Phys.* **34**, 1476 (1961). J. Tang and A. C. Albrecht, in *Raman Spectroscopy*, edited by H. A. Szymanski (Plenum Press, New York, 1970), Vol. 2, p. 207.

⁴ Refer to the following paper for the experimental method: K. Kaya, N. Mikami, Y. Udagawa, and M. Ito, *Chem. Phys. Letters* **13**, 221 (1972).

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Ion-Pair Production of O⁺ and O⁻ from O₂ by He(2¹S, 2³S) Metastables

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In addition to the usual Penning ionization of O₂ by He(2¹S) and He(2³S) metastable atoms



ion-pair production of O⁺ and O⁻



is energetically possible since the ion-pair appearance potential of 17.3 eV lies below the 20.6 and 19.8 eV energies of the He(2¹S) and He(2³S) metastables. We wish to report in this Communication that Reaction (2) has been observed both in a flowing afterglow and a beam apparatus.

The flowing afterglow apparatus has been described in detail elsewhere¹ and it suffices to state here that a mixture of He(2¹S) and He(2³S) metastables were formed in the helium buffer gas by electron impact at accelerating voltages below the ionization potential of helium. A small flow of O₂ was added downstream and the resulting positive and negative ions were sampled further downstream by a quadrupole mass spectrometer. SF₆ was added between the helium and oxygen inlets to attach the electrons formed from Reaction (1). The resulting positive-ion-negative-ion plasma (as opposed to a positive-ion-electron plasma) improved the sampling of the negative ions.

In addition to the usual O₂⁺ formed by Reaction (1), approximately equal O⁺ and O⁻ signals were observed and were more than an order of magnitude smaller than the O₂⁺ intensity. Rate constants were determined from the increase in the O₂⁺, O⁺, and O⁻ signals as a function of increasing O₂ flow. The resulting values were between the 5.8 × 10⁻¹⁰ and 2.1 × 10⁻¹⁰ cm³/molecule-sec reported for the Penning ionization of O₂ by He(2¹S) and He(2³S) metastables, respectively.² This similarity demonstrates that all three of these products are the result of the same first-order process, namely, the destruction of He(2¹S, 2³S) metastables. In particular, this eliminates the possibility that the O⁻ ions are the result of dissociative attach-

ment of electrons on O₂, which would be second order in the oxygen density. The relative magnitudes of the O⁺ or the O⁻ and the O₂⁺ densities, although not accurately known, shows that the rate of Reaction (2) is substantially smaller than that of Reaction (1).

Reaction (2) was also observed in a beam apparatus very similar to the one described earlier.³ Helium was bombarded by electrons at 50 eV energy and the extraction of the charged products and the removal of highly excited atoms⁴ produced a neutral beam containing ground state and metastable helium atoms. The He(2¹S) metastables could be quenched by a quartz, spiral-shaped, helium-discharge lamp surrounding the beam. In this way, either a "mixed" He(2¹S)/He(2³S) or a "pure" [less than 2% He(2¹S)] He(2³S) beam could be utilized. Positively and negatively charged products from the reaction of this beam on O₂ were analyzed in a magnetic mass spectrometer.

In addition to the O₂⁺ ions from Reaction (1), O⁺ and O⁻ ions were produced both by the "mixed" and the "pure" beam. The observation of O⁻ confirms the existence of the ion-pair Reaction (2) since dissociative attachment is no problem here and Reaction (2) is the only channel energetically possible for O⁺ and O⁻ production. Because the relative detection efficiencies were not known, a method other than a direct comparison of the O⁺ and O⁻ signals was used to show that the cross sections for the production of O⁺ and O⁻ are equal. The ratio of the product ion current using a "mixed" beam to that for a "pure" beam was taken for both O⁻ and O⁺. These ratios ($I_{\text{mixed}}/I_{\text{pure}}$) depend on the cross sections q_s and q_t for ion production by He(2¹S) and He(2³S), as well as the number densities N_s and N_t of the metastables

$$I_{\text{mixed}}/I_{\text{pure}} = (N_s q_s / N_t q_t) + 1. \quad (3)$$

It was found that the ratios were equal for O⁺ and O⁻ production, which implies

$$q_s(\text{O}^+)/q_t(\text{O}^+) = q_s(\text{O}^-)/q_t(\text{O}^-). \quad (4)$$