

Calculation of Cl₂ vibrational distributions after vibrational predissociation of He₂-Cl₂

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A wave-packet description of the vibrational predissociation (VP) dynamics of He₂-Cl₂(*B*, *v*') including six-coupled degrees of freedom was recently reported.¹ Good agreement was found between the calculated and experimental^{2,3} predissociation lifetimes and Cl₂ fragment rotational distributions for the *v*'=10-13 initial vibrational excitations of Cl₂ probed experimentally. However, the calculated Cl₂ product vibrational distributions were in clear disagreement with the trend expected from measurements of these distributions for He₂-Cl₂(*B*, *v*'=8) predissociation.³ Specifically, the calculated population of the Δ*v*'=-1 dissociation channel was found to be overestimated at the expense of the population of the Δ*v*'<-1 channels. The discrepancy was attributed to an artifact in the calculation of the vibrational distributions, due to the use of absorbing boundary conditions and finite grid limitations. Such limitations cause that wave packet components corresponding to He+He-Cl₂ are absorbed before complete dissociation to He+He+Cl₂ takes place.

It was argued¹ that a rigorous way to minimize the above artifact is to use large grids in the dissociative coordinates, placing the absorbing boundary conditions as far as possible in the asymptotic region. Unfortunately, at present this alternative is out of reach for a full-dimensional tetra-atomic system like He₂-Cl₂. Thus, it would be very desirable to have an available approximate but reliable enough model which, using reasonable grid sizes, is able to provide realistic estimates for the vibrational distributions. The purpose of this work is to suggest and test one such model.

Wave-packet simulations of the He₂-Cl₂(*B*, *v*') VP dynamics were carried out for the *v*'=8, 10, and 12 vibrational excitations of Cl₂. Details of the dynamical method and the simulation have been described elsewhere.¹ The only difference is that here the wave packet is propagated up to a longer final time *t_f*=6.5 ps. In order to calculate the Cl₂ fragment vibrational distributions, the following approximate model was applied based on a previously suggested approach.⁴ The probability of the different vibrational dissociation channels at time *t* is expressed as

$$P_{v'}(t) = P_{v'}^P(t) + (1 - Q_{v'}^C)P_{v'}^C(t), \quad (1a)$$

$$P_{v'-1}(t) = P_{v'-1}^P(t) + Q_{v'}^C R_{v' \rightarrow v'-1} P_{v'}^C(t) + (1 - Q_{v'-1}^C)P_{v'-1}^C(t), \quad (1b)$$

$$P_{v'-2}(t) = P_{v'-2}^P(t) + Q_{v'}^C R_{v' \rightarrow v'-2} P_{v'}^C(t) + Q_{v'-1}^C R_{v'-1 \rightarrow v'-2} P_{v'-1}^C(t) + (1 - Q_{v'-2}^C)P_{v'-2}^C(t), \quad (1c)$$

$$P_{v'-3}(t) = P_{v'-3}^P(t) + Q_{v'}^C R_{v' \rightarrow v'-3} P_{v'}^C(t) + Q_{v'-1}^C R_{v'-1 \rightarrow v'-3} P_{v'-1}^C(t) + Q_{v'-2}^C R_{v'-2 \rightarrow v'-3} P_{v'-2}^C(t) + (1 - Q_{v'-3}^C)P_{v'-3}^C(t). \quad (1d)$$

The above equations consider four vibrational channels, *v*', *v*'-1, *v*'-2, and *v*'-3, since these are the channels included in the wave-packet simulations,¹ but the model can be easily generalized to as many vibrational channels as desired. In Eqs. (1), *P_v^P*(*t*) and *P_v^C*(*t*) are the accumulated probabilities in the regions of the grid *P* and *C*, respectively. The region *P* is defined as *R*₁, *R*₂ > 16.5 a.u., being *R*₁ and *R*₂ the coordinates associated with the distance between each He atom, respectively, and the Cl₂ center of mass. The distance of 16.5 a.u. is taken as that for which each van der Waals bond is considered effectively broken. The region *C* corresponds to the grid portions *R*₁ < 16.5 a.u., *R*₂ ≥ *R*_{abs} = 28.0 a.u. and *R*₁ ≥ *R*_{abs} = 28.0 a.u., *R*₂ < 16.5 a.u., i.e., this is the region where the wave-packet components corresponding to He+He-Cl₂ intermediate products are absorbed.

The *Q_v^C* quantities denote the fraction of the absorbed probability *P_v^C*(*t*) which populates quasibound states of the intermediate products He+He-Cl₂(*B*, *v*) that will decay to He+He+Cl₂(*B*, *v*' < *v*). The fraction (1 - *Q_v^C*) in the *v* channel would correspond to direct scattering processes leading to He+He+Cl₂(*B*, *v*) without changing *v*. A rigorous calculation of *Q_v^C* would involve to project out the wave packet absorbed in region *C* onto all the quasibound states of the intermediate He+He-Cl₂(*B*, *v*) products. For a six-dimensional wave packet such a calculation is out of reach. In the present model it is assumed that *Q_v^C* = *Q_{v'-1}^C* = *Q_{v'-2}^C* = *Q_{v'-3}^C* = 1, meaning that all the probability *P_v^C*(*t*) of He+He-Cl₂(*B*, *v*) components absorbed would dissociate to He+He+Cl₂(*B*, *v*' < *v*) if they were not absorbed.

The *R_{v→v''}* quantities stand for the percentage of the *P_v^C*(*t*) probability absorbed in channel *v* going to the lower vibrational channels *v*'. Again, to be rigorous, the *R_{v→v''}* values should be those corresponding specifically to each popu-

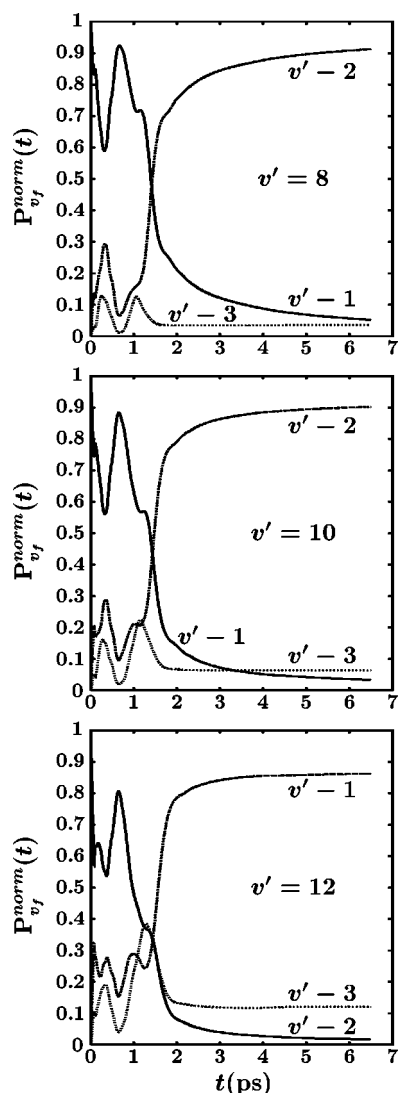


FIG. 1. Time evolution of the normalized vibrational populations of the $\text{Cl}_2(B, v_f)$ fragment ($v_f = v' - 1$, $v' - 2$, and $v' - 3$) for the initial Cl_2 vibrational excitations v' studied.

lated quasibound state of the $\text{He} + \text{He} - \text{Cl}_2(B, v)$ intermediate products. In the model the $R_{v \rightarrow v''}$ values are taken from the vibrational distributions calculated for VP from the ground resonance state of the $\text{He} - \text{Cl}_2(B, v)$ system in Ref. 5, in the assumption that they do not change much for other quasibound states.

The $P_v(t)$ probabilities obtained with Eqs. (1a)–(1d) are normalized to give

$$P_{v_f}^{\text{norm}}(t) = \frac{P_{v_f}(t)}{\sum_v P_v(t)}, \quad (2)$$

where $v_f = v' - 1$, $v' - 2$, and $v' - 3$. After sufficient propagation time, the $P_{v_f}^{\text{norm}}(t)$ probabilities stabilize and provide an estimate of the Cl_2 fragment vibrational populations.

The present model is similar to that proposed in Ref. 4, which is inspired in the nature of the vibrational predissociation process consisting of the decay of intensity from the initial state v' to lower vibrational dissociation channels. The main difference between the current and the earlier model is the explicit inclusion of the $R_{v \rightarrow v''}$ quantities in Eqs. (1), which are expected to make the model more flexible.

TABLE I. Calculated and experimental $\text{Cl}_2(B, v_f)$ fragment vibrational populations (in percentage) after predissociation through the channels $v_f = v' - 1$, $v' - 2$, and $v' - 3$.

	v'	$v' - 1$	$v' - 2$	$v' - 3$
This work	8	5.2	91.3	3.5
	10	3.4	90.3	6.3
	12	1.7	86.2	12.1
Experiment ^a	8	8	92	<1

^aReference 3.

In Ref. 1 the vibrational probabilities were calculated as $P_v(t) = P_v^P(t)$, i.e., neglecting the absorbed wave packet intensity $P_v^C(t)$. However, $P_v^C(t)$ is much larger than $P_v^P(t)$, and thus neglecting $P_v^C(t)$ causes large errors in the final Cl_2 vibrational populations. Using the $P_v^C(t)$ and $P_v^P(t)$ probabilities calculated from the wave-packet dynamical simulation as input for Eqs. (1) and (2), the evolution of $P_{v_f}^{\text{norm}}(t)$ with time is obtained, and it is shown in Fig. 1 for the three vibrational decay channels considered, for the three v' initial states studied. The figure shows that $P_{v_f}^{\text{norm}}(t)$ is sufficiently stabilized at $t = 6.5$ ps as to obtain an estimate for the vibrational populations. Such populations are collected in Table I. The agreement with the experimental values (available only for $v' = 8$) is quite good, despite the assumptions of the model. In addition, the expected trend is found for the populations as v' increases, namely a gradual decrease of the $v' - 1$ and $v' - 2$ populations, and an increase of the $v' - 3$ channel probability. For all the v' initial states studied the $\Delta v' = -2$ dissociation channel is found to be the dominant one, consistent with a mainly sequential fragmentation mechanism.^{1,2}

In conclusion, this work tests an approximate model to obtain vibrational distributions of the Cl_2 fragment produced after $\text{He}_2 - \text{Cl}_2(B)$ predissociation, when the dynamics is simulated by a full-dimensional wave-packet method. The model is intended to overcome the limitations imposed to a rigorous calculation of the vibrational distributions by the use of a finite grid size and absorbing boundary conditions, which are required to make the quantum-mechanical simulation tractable. The good agreement found between the present results and the available experimental data indicates that the model is able to provide realistic estimates for the diatomic product vibrational distributions. Application of this model in simulations of the vibrational predissociation dynamics of other tetra-atomic complexes is therefore envisioned.

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¹A. García-Vela, J. Chem. Phys. **122**, 14312 (2005).

²M. I. Hernández, N. Halberstadt, W. D. Sands, and K. C. Janda, J. Chem. Phys. **113**, 7252 (2000).

³W. D. Sands, C. R. Bieler, and K. C. Janda, J. Chem. Phys. **95**, 729 (1991).

⁴F. Le Quéré and S. K. Gray, J. Chem. Phys. **98**, 5396 (1993).

⁵A. García-Vela, J. Chem. Phys. **119**, 5583 (2003).