

## Communications: A model study on the electronic predissociation of the NeBr<sub>2</sub> van der Waals complex

Cristina Sanz-Sanz,<sup>1,a)</sup> Octavio Roncero,<sup>1,b)</sup> Ramón Hernández-Lamoneda,<sup>2</sup> Jordan M. Pio,<sup>3</sup> Molly A. Taylor,<sup>3</sup> and Kenneth C. Janda<sup>3</sup>

<sup>1</sup>Instituto de Física Fundamental, CSIC, Serrano 123, Madrid 28006, Spain

<sup>2</sup>Centro de Investigaciones Químicas, Universidad Autónoma de Morelos, Avenida Universidad 1001, Cuernavaca, Morelos 62210, Mexico

<sup>3</sup>Department of Chemistry, University of California, Irvine, California 92697, USA

(Received 7 April 2010; accepted 26 April 2010; published online 10 June 2010)

Recently, the predissociation lifetimes of the NeBr<sub>2</sub>(B) complex for different initial vibrational excitation ( $10 \leq v' \leq 20$ ) have been measured using time-resolved optical pump-probe spectroscopy [Taylor *et al.*, *J. Chem. Phys.*, **132**, 104309 (2010)]. In the vibrational interval studied, the vibrational predissociation (VP) proceeds by the transfer of a single vibrational quantum and the lifetimes are expected to decrease smoothly with increasing  $v'$ , as predicted by the energy gap law. However, the experimental lifetimes show strong oscillations with  $v'$ , which were attributed to the occurrence of electronic predissociation into two possible dissociative electronic states of Br<sub>2</sub>(1<sub>g</sub>, 2<sub>g</sub>), based on a Franck–Condon spectator model. In this work we reproduce the experimental findings by performing full three-dimensional wave packet calculations for the competition of vibrational and electronic predissociation, including the B(0<sub>u</sub><sup>+</sup>), 2<sub>g</sub>, and C(1<sub>u</sub>) electronic states. Model potential energy surfaces were used based on previous theoretical simulations of the VP dynamics on the B state and on *ab initio* calculations on the NeCl<sub>2</sub> related system. Thus, only two parameters, the strength of the electronic couplings, are fit to achieve the excellent theoretical/experimental agreement. © 2010 American Institute of Physics. [doi:10.1063/1.3429940]

The noble gas-halogen dimers have provided a rich model system for investigating van der Waals interactions and energy transfer processes. Since the vibrations on each monomer are nearly independent, it is possible to follow the energy flow from the halogen stretch degree of freedom to the van der Waals degrees of freedom. One issue for which experiment and theory have yet to converge is the competition between vibrational dynamics and electronic dynamics. Typically, the electronic predissociation (EP) corresponds to dark channels yielding halogen atoms in the ground electronic state, and only the vibrational predissociation (VP) dynamics is directly monitored through the laser-induced fluorescence of the diatomic halogen fragment.

That such competition exists was first realized for the Ar<sub>n</sub>-I<sub>2</sub> molecules.<sup>1,2</sup> Burke and Klemperer<sup>3</sup> measured the VP/EP relative efficiency for  $v'=16-23$  of ArI<sub>2</sub> and concluded that the observed oscillations are due to EP, while the VP rate may increase monotonically with  $v'$ . Since total decay rates have only been measured for  $v'=18$  and 21 (Ref. 4), it is not yet possible to know the values of the independent VP and EP rates. The oscillations of the EP rate were confirmed theoretically using a time dependent Golden rule treatment for EP.<sup>5</sup> However, this simple picture of the VP/EP competition was challenged when it was realized that the VP dynamics occurs by the transfer of two or three vibrational

quanta via intramolecular vibrational energy relaxation (IVR) in the sparse-intermediate regime,<sup>6</sup> yielding VP rates which oscillate more drastically than the EP rates. This was later confirmed by full quantum wave packet calculations<sup>7,8</sup> on the competition between VP and EP dynamics, as recently reviewed.<sup>9</sup> Thus the details of the competition between VP and EP in ArI<sub>2</sub> remain an open problem.

For the noble gas Cl<sub>2</sub> species, the occurrence of EP has been inferred from the sudden decrease in the fluorescence signal due to VP products as  $v'$  increases. No laser excited fluorescence or pump-probe signals were observed for the Ar-Cl<sub>2</sub> B-state vibrational levels  $v' > 12$ ,<sup>10</sup> which was ascribed to EP dynamics between the B and C(1<sub>u</sub>) states of chlorine. For HeCl<sub>2</sub>, the signals due to VP became unobservable above  $v'=24$ .<sup>11</sup> For NeCl<sub>2</sub>, the signals due to VP are quite weak above  $v'=16$ .<sup>12</sup> Recently, the first detailed *ab initio* calculations on the nature of the electronic states involved in the EP process were performed on the NeCl<sub>2</sub> system.<sup>13</sup> This study showed that the electronic state involved is of 2<sub>g</sub> symmetry in the Cl<sub>2</sub> monomer. Wave packet calculations<sup>12</sup> on the NeCl<sub>2</sub> and ArCl<sub>2</sub> systems showed that, indeed, the 2<sub>g</sub> state is responsible for the competition between EP and VP processes. On the other hand, the theoretical simulations could not reproduce accurately the disappearance of the fluorescence, proving the EP/VP competition remains a challenging problem for *ab initio* calculations.

For the heavier noble gas species, Kr and Xe-Cl<sub>2</sub> (Refs. 14 and 15) weak pump-probe signals due to VP were observed for only a few vibrational levels. In these cases, the highest vibrational level observed is even lower than for

<sup>a)</sup>Present address: School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom.

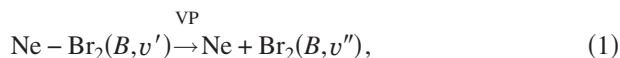
<sup>b)</sup>Author to whom correspondence should be addressed. Electronic mail: roncero@iff.csic.es.

Ar-Cl<sub>2</sub>, probably due to the fact that the heavier noble gas atoms enhance the coupling between the B and C(1<sub>u</sub>) states, making the EP channel the dominant one.

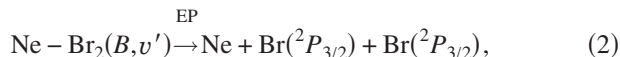
Very recently, the fragmentation lifetimes of NeBr<sub>2</sub>(B) for different initial vibrational excitation ( $10 \leq v' \leq 20$ ) were measured using time-resolved optical pump-probe spectroscopy.<sup>16</sup> In the vibrational interval studied, the VP proceeds by the transfer of a single vibrational quantum, and the lifetimes are expected to decrease smoothly with increasing  $v'$ , as predicted by the energy gap law. This is in contrast with ArI<sub>2</sub> VP, where IVR complicates the analysis. However, the experimental lifetimes of the NeBr<sub>2</sub>(B) show strong oscillations with  $v'$ , which were attributed to the occurrence of EP into several dissociative electronic states of Br<sub>2</sub>. The 1<sub>g</sub>/2<sub>g</sub> states were identified as the dissociative states primarily responsible for the EP, based on a Franck-Condon spectator model.<sup>16</sup> Thus, many of the features of the EP process depend upon the identity of the noble gas atom and the halogen. Franck-Condon factors and EP channel openings are determined by where the dissociative states (correlating to X(<sup>2</sup>P<sub>3/2</sub>) + X(<sup>2</sup>P<sub>3/2</sub>)) cross the B state (correlating to X(<sup>2</sup>P<sub>3/2</sub>) + X(<sup>2</sup>P<sub>1/2</sub>)). For Cl<sub>2</sub>, this crossing is near the B-state dissociation limit due to the small spin-orbit splitting of the two asymptotic limits. As this spin-orbit splitting increases for Br<sub>2</sub> and I<sub>2</sub>, the crossings move toward the bottom of the B-state well. Increasing the size of the noble gas atom enhances the electronic coupling through the strengthening of the van der Waals interactions and also increases the likelihood that EP and IVR will be in competition. NeBr<sub>2</sub> is therefore an ideal case because (1) the VP dynamics is expected to be simple due to the absence of IVR, and (2) the VP and EP rates are of a similar order of magnitude so that the two processes compete and fragmentation can be probed by detecting Br<sub>2</sub>(B) fragments. All these features make NeBr<sub>2</sub> an ideal system for studying the competition between these two processes.

In this work, three-dimensional quantum dynamics of the fragmentation dynamics of NeBr<sub>2</sub> is studied, including EP and VP channels. The aim is to explain the oscillations of the lifetimes measured as a function of the NeBr<sub>2</sub>(B,  $v'$ ) vibrational level initially excited and to confirm the Franck-Condon model assumed by Taylor *et al.*<sup>16</sup>

For the description of the competition between the VP,



and the EP dynamics



three-dimensional wave packet (WP) calculations are performed for zero total angular momentum  $J=0$ , and using Jacobi coordinates, as described in detail previously.<sup>8</sup> The internal coordinates used are  $r$  the Br<sub>2</sub> internuclear distance,  $R$  is the distance from the Br<sub>2</sub> center-of-mass to the Ne atom, and  $\gamma$  is the angle between the vectors associated with  $r$  and  $R$ . The wave packet is represented in a grid for the internal coordinates,  $r, R, \gamma$  (with  $\cos \gamma = \mathbf{r} \cdot \mathbf{R} / rR$ ) and zero total angular momentum  $J=0$ . A two-dimensional grid of 256  $\times$  160 points is used for the radial variables in the intervals

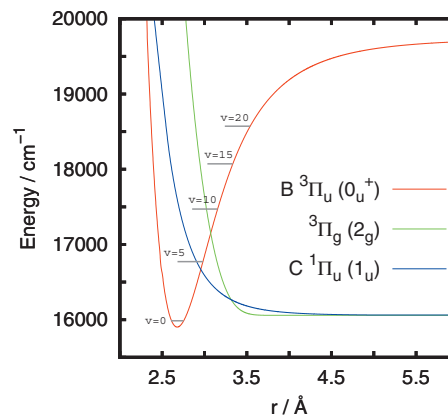


FIG. 1. Potential energy curves used to describe Br<sub>2</sub> in the B (Ref. 17), 2<sub>g</sub> (Refs. 18 and 19), and C (Refs. 20 and 21) states.

$1.5 < r < 7$  Å and  $2.5 < R < 18$  Å. The angle  $\gamma$  is described by 35 Gauss-Legendre quadrature points in the interval  $[0, \pi/2]$ . A Chebyshev propagator is used, with a time interval of 20 fs up to  $\approx 500$  ps. After each time step, the wave packet is multiplied by an absorbing Gaussian for  $r > 5$  Å and  $R > 15$  Å, with exponential constants of 0.05 and 0.025 for  $r$  and  $R$ , respectively.

The electronic part of the Hamiltonian is represented by a  $3 \times 3$  diabatic matrix,  $H^e$ , corresponding to the B(<sup>3</sup>Π<sub>u</sub>[0<sub>u</sub><sup>+</sup>]), <sup>3</sup>Π<sub>g</sub>(2<sub>g</sub>), and C(<sup>1</sup>Π<sub>u</sub>[1<sub>u</sub>]) states. The diagonal terms are built as the sum of two contributions,

$$H_{ii}^e = V_i(r) + W(r, R, \gamma), \quad (3)$$

where  $V_i$  ( $i=B, 2_g, C$ ) are the Br<sub>2</sub> diatomic curves and  $W$  describes the Ne-Br<sub>2</sub> van der Waals interaction. The Br<sub>2</sub> B state is taken from the Rydberg-Klein-Rees (RKR) potential of Barrow *et al.*,<sup>17</sup> the Br<sub>2</sub>(2<sub>g</sub>) potential energy surface (PES) is taken from Refs. 18 and 19 and that of the Br<sub>2</sub>(C) by Tellinghuisen.<sup>20,21</sup> All of them are shown in Fig. 1

From our previous studies on the NeCl<sub>2</sub> complex<sup>12,13</sup> we know that the van der Waals interaction potential  $W$  is quite similar for the different electronic states, and for this reason the same functional form is used for all of them. In this case, we use the potential developed in Ref. 22 to reproduce the binding energies and bond length of NeBr<sub>2</sub> complexes and used later on to describe the VP dynamics.<sup>23,24</sup> This PES consists of a sum of two pairwise Ne-Br Morse potentials, with the parameters  $D=42$  cm<sup>-1</sup>,  $\alpha=1.67$  Å<sup>-1</sup>, and  $R_e=3.9$  Å.

The B-2<sub>g</sub> nondiagonal matrix element is represented by

$$V_{B/2g}(r, R, \gamma) = \Delta_{B/2g} e^{-\beta(R-\rho_e)} \sin \gamma \cos^2 \gamma, \quad (4)$$

where the angular dependence is analogous to that obtained for ArI<sub>2</sub> using a Diatomics-in-Molecules (DIM) model.<sup>9</sup> This functional form fits very well the available *ab initio* calculations obtained for Ne-Cl<sub>2</sub>.<sup>12</sup> The B/C(1<sub>u</sub>) coupling presents a different angular dependence (see Fig. 2 of Ref. 7, and note that for I<sub>2</sub> the 1<sub>u</sub> state is called B''). However, around the T-shape configuration, where the amplitude of the initial state is nonzero, the B/2<sub>g</sub> and B/C(1<sub>u</sub>) show a similar angular dependence. For this reason, the same functional form is used to describe the B-C coupling, but with a different  $\Delta_{B/C}$

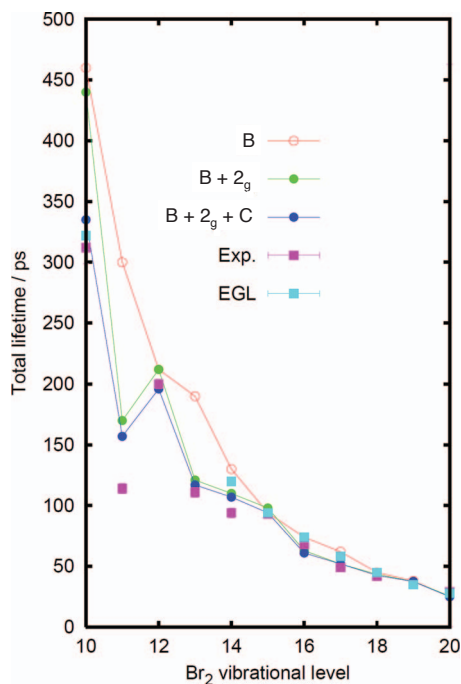


FIG. 2. Lifetimes (in picosecond) as a function of initial vibrational excitation of Br<sub>2</sub> obtained for (a) only the B state, (b) the B and 2<sub>g</sub> states, (c) the B, 2<sub>g</sub>, and C states, (d) the experimental values of Ref. 16, and (e) the energy gap law fit from Ref. 16.

factor. In fact, these two constants  $\Delta_{B/2g}=400\text{ cm}^{-1}$  and  $\Delta_{B/C}=100\text{ cm}^{-1}$  are the only parameters optimized in this work to fit the experimental lifetimes.  $\rho_e=3.6\text{ \AA}$  approximately corresponds to the intermolecular equilibrium distance of the complex. The  $\beta=2.8\text{ \AA}^{-1}$  value was taken from the previous fit performed to *ab initio* points for the NeCl<sub>2</sub> system.<sup>12</sup> Finally, the 2<sub>g</sub>-C coupling is neglected, since it does not play any fundamental role in the EP dynamics from the B state.

The initial wave packet is constructed for studying the VP/EP dynamics in the so-called bright approximation which corresponds to a bound state calculated for the isolated B electronic state and one single vibrational Br<sub>2</sub> function  $v'$ , as described previously for ArI<sub>2</sub>.<sup>8</sup> This approximate bound state defines the initial state, which decays on the different dissociation channels. The total decay of each initial state is fitted to an exponential of the form  $\exp[-t/\tau]$ , which agrees very well with the numerical calculations. The  $\tau$  thus obtained determine the total lifetime of the system.

To identify the contributions of the B, 2<sub>g</sub>, and C electronic states to the fragmentation dynamics, three different calculations were performed, each distinguished by the electronic states included: (1) B, (2) B+2<sub>g</sub>, and (3) B+2<sub>g</sub>+C. The results are shown in Fig. 2 and compared with the experimental values of Ref. 16.

When only the B state is included, the predissociation occurs solely through VP, and the lifetime decreases monotonically with increasing  $v'$ . The behavior of  $\tau$  with  $v'$  is not as smooth as predicted by the energy gap law,<sup>16</sup> which is also included in the figure with the label EGL. The small anomalies may arise from the inaccuracies of fitting procedure followed or to the occurrence of some IVR with overbarrier

resonances of the  $v-1$  manifold. The present results in general are in very good agreement with previously reported time-independent (TI) calculations that used the same potential,<sup>23</sup> with the lifetimes differing by 1-3 ps. The exception is  $v'=10$ , for which the TI results is 394 ps versus 462 ps in the present study. The present WP results use exactly the same grid (or Hamiltonian representation) for all the initial  $v'$ , and the only difference among the different calculations corresponds to the initial state used at  $t=0$ . This important difference reported for the case is attributed to numerical differences between TI and WP calculations and different parametrization. Note, however, that the EGL fit shown in Fig. 2 is taken from Ref. 16, where the experimental lifetime of  $\tau=312\text{ ps}$  was used in the determination of the EGL fit parameters instead of the 462 ps VP lifetime found in this work.

When the 2<sub>g</sub> state is included, EP also takes place, and the lifetime shows a dip for  $v'=11$ . As noted in Ref. 16 this is the result of the Franck-Condon factors between the B and 2<sub>g</sub> state of the pure diatomic Br<sub>2</sub> system. At  $v'=11$  and 13 the overlap is maximal, and the EP process becomes significant, producing shorter lifetimes than those obtained by VP alone. The good agreement in the oscillations between theoretical and experimental results demonstrate that the origin of the experimental oscillation is indeed the appearance of EP into the 2<sub>g</sub> state.

The largest disagreement is for  $v'=10$ , for which the theoretical results predict a much longer lifetime than was measured. This disagreement is attributed to EP into the C state (shown in Fig. 1), which crosses the B state at lower energies than the 2<sub>g</sub> state. Thus, when this channel is included, the lifetime of the  $v'=10$  decreases significantly, while the lifetimes of higher  $v'$  levels change only slightly, so that the agreement with the experimental values is satisfactory. Note that the lifetime obtained previously for  $v'=10$  (Ref. 23) is in better agreement with the experimental value. This may suggest that the B/C coupling could be reduced significantly.

The present simulations based on realistic model potential energy surfaces corroborate the origin of the oscillations in the total decay lifetimes for the NeBr<sub>2</sub> system as being attributed to EP into the 2<sub>g</sub> and C dissociative states. The good agreement was obtained by the adjustment of only two parameters, the magnitude of the electronic couplings, and physically reasonable values for these couplings were used to achieve the good agreement. Moreover, the van der Waals potential used for the B state was fit to reproduce the experimental binding energy and bond length of the NeBr<sub>2</sub> complex for several vibrational states. For this purpose, the Morse parameters  $D$  and  $R_e$  were adjusted.<sup>22</sup> The parameter  $\alpha$  was kept fixed, and it is this parameter of the potential which affects the most the VP lifetimes. Therefore, a refit of this parameter of the potential could yield an improvement in the comparison with experimental results, especially if the EP process is also accounted for.

At this point, *ab initio* calculations are needed to definitively establish the PESs and couplings involved. Such calculations are difficult to perform with the desired accuracy. They involve excited electronic states, for which multirefer-

ence methods are needed, and weak interactions, for which size-consistent methods are needed. However, these kinds of calculations are of great help in determining the adequacy of the different assumptions required to perform a model electronic Hamiltonian for this system, and some work in this direction is being conducted. In addition, a similar study applied to the HeBr<sub>2</sub> complex is now in progress.

The measurement of the total lifetimes over a wide range of vibrational levels performed in the NeBr<sub>2</sub> system allows for the establishment of a simple elegant model for the VP/EP competition. Similar measurements would be of great help for the ArI<sub>2</sub> system, for which only  $v'=18$  and 21 have been measured. With the total lifetimes, it would be possible to assign the origin of the oscillations of the VP/EP relative efficiency measured by Burke and Klemperer,<sup>3</sup> for which there is still some controversy.<sup>9</sup>

In addition, a similar study for Ne<sub>2</sub>Br<sub>2</sub> would be interesting since the EP rates scale quadratically while VP rates should scale approximately linearly with the number of Ne atoms. In this last case, if we consider that the Ne<sub>2</sub>Br<sub>2</sub> has a larger binding energy, the available kinetic energy decreases. According to the energy gap law, the VP rate can increase faster than linearly when this effect is taken into account. This last effect is especially important near thresholds, where the change in available kinetic energy is more significant.

## ACKNOWLEDGMENTS

This work has been supported by the Ministerio de Ciencia e Innovación under Project No. CTQ2007-62898 and U.S. National Science Foundation Grant No. CHE-0404743. The calculations have been performed in the IFF and CESGA computing centers.

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