Vibrational predissociation of NeBr_2 ($X, v=1$) using an *ab initio* potential energy surface

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Quantum mechanical calculations on the vibrational predissociation dynamics of NeBr_2 are performed using an *ab initio* (coupled cluster using single and double excitations with a noniterative perturbation treatment of triple excitations) potential energy surface. Energy positions, lifetimes, and final rotational state distributions are determined for vibrational predissociation from the two lowest linear ($n=0$) and T-shaped ($n=1$) van der Waals levels of NeBr_2 ($X, v=1$). Comparison with the experimental assumption as regards the energy transfer to rotation provides information about the type of isomer involved in the experimental vibrational predissociation process, suggesting that it was the linear one. © 2002 American Institute of Physics. [DOI: 10.1063/1.1519001]

I. INTRODUCTION

van der Waals (vdW) complexes of rare gas atoms with halogen and interhalogen molecules have attracted a lot of attention both experimental and theoretical.^{1,2} The relative simplicity of these species allows for a quantitative comparison between theory and experiment and serves to enhance our understanding on intermolecular vibrational energy transfer and fragmentation dynamics processes.

For such complexes the experiments can be performed at the state-to-state level. For instance, using pump-probe spectroscopy a specific initial level of the rare gas-halogen complex in the electronically excited state, usually the B one, can be populated and the products of vibrational predissociation (VP) of this level can be detected yielding rate and product state distribution.^{3,4} Quantum calculations are also capable of providing rigorous results comparable with the experiment.

A difficulty in the theoretical analysis of such data is the construction of quantitatively accurate potential energy surfaces (PESs). Until recently, in most of the dynamical studies of rare gas-halogen complexes pairwise additive PESs have been employed. Even though the atom-atom potentials have been widely used, they have not been able to reproduce the high anisotropy of van der Waals complexes and to describe accurately enough all details of their dynamics.⁵⁻⁷ In particular, the atom-atom potentials give T-shaped structures for rare gas-halogen complexes in the ground electronic state, whereas recent spectroscopic data,^{8,9} some semiempirical^{10,11} and high level *ab initio* calculations¹²⁻¹⁶ predicting the existence of linear structures on the ground PESs of these complexes. *Ab initio* electronic structure calculations have become gradually more accurate and they are now powerful enough to be used for interpreting experimental data of rare gas-dihalogen complexes.^{12,17}

The problem of the topology of the ground rare gas-dihalogen PESs is challenging for the general theory of intermolecular interactions.¹ One of the goals of theoretical studies is to assist the experimental search and assignment of the signatures of different isomers. According to recent *ab initio* and semiempirical calculations,¹⁸⁻²¹ the PES of excited B state has the main minimum in the T-shaped configuration and only very shallow well in the collinear geometry. As a result, excitation of the ground state linear isomer yields either continuous absorption⁸ or quasidiscrete transitions to excited van der Waals levels of the B state.^{7,9,17} The measured VP rates and product state distributions mirror the properties of the initial linear complex only indirectly. Thus, for studying the linear isomers directly, the ground-state complexes should be investigated. From the experimental viewpoint such measurements are very difficult. To our knowledge, only the $\text{NeBr}_2(X)$ complex has been studied so far.²² Analyzing the excitation spectrum intensity ratio of the complex and bare bromine molecule in the molecular beam as a function of the distance from the nozzle, Janda and co-workers were able to determine the lifetime of the $\text{NeBr}_2(X, v=1)$ complex. According to very recent *ab initio* calculations,¹⁵ the ground-state PES of the NeBr_2 complex has a deep well in the linear configuration. The two lowest van der Waals energy levels, $n=0$ and $n=1$, correspond to linear and T-shaped isomers, respectively, and are separated by $\sim 5 \text{ cm}^{-1}$.

The purpose of the present paper is to study the vibrational predissociation of the $\text{NeBr}_2(X)$ complex with $v=1$ vibrational excitation for the Br_2 stretch mode and with $n=0$ and 1 for the vibrational vdW modes, using a three-dimensional (3D) CCSD(T) (coupled-cluster with single, double and a noniterative perturbation treatment of triple excitations) *ab initio* potential. Golden rule and full 3D quantum calculations are carried out to obtain lifetimes, resonance line shapes, and final state product distributions. Comparing our results with the available experimental data the main features which distinguish the fragmentation dynamics of linear and T-shaped isomers can be established.

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The paper is organized as follows: In Sec. II we discuss our *ab initio* results. In Sec. III we present the parametrized potential energy surfaces and our results, based on Golden rule and line shape calculations, on the vibrational predissociation dynamics of $\text{NeBr}_2(X)$ are compared with experimental measurements. Some conclusions constitute the closing section.

II. AB INITIO COMPUTATION

We use Jacobi coordinates (r, R, θ) to describe the potential energy surface of NeBr_2 complex, where R is the intermolecular distance of Ne atom from the center of mass of Br_2 , r is the bond length of Br_2 , and θ is the angle between the $\mathbf{R}$ and $\mathbf{r}$ vectors. Intermolecular energies are calculated for several R distances ranging from $R=2.5$ to $10 \text{ \AA}$, for each of the following five angles: $\theta=0^\circ, 30^\circ, 45^\circ, 60^\circ, 90^\circ$, and for five different Br_2 bond-lengths: $r=2.0998, 2.1733, 2.281, 2.3887, 2.4622 \text{ \AA}$. The r values are chosen around the equilibrium distance of $r_e=2.281 \text{ \AA}$ in a range that is enough to describe the first two excited vibrational levels of Br_2 .

The *ab initio* calculations are performed using the GAUSSIAN 98 package.²³ For the present calculation of the NeBr_2 potential we use effective core potentials basis set for Br atoms, that is a convenient method to incorporate relativistic effects^{24,25} in standard quantum mechanical calculations. We employ the Stuttgart group (SDD) effective core potential²⁶ augmenting its valence part with (*sp*) diffusion and (*3df*) polarization functions, SDD+G(*3df*),²⁷ for bromine atoms. Recent studies have shown,^{15,28–31} that the use of midbond functions is an efficient way to saturate the dispersion energy, the dominant attractive force in the case of van der Waals complexes. Thus, the augmented correlation consistent aug-cc-pVQZ basis set for Ne atom, incorporated in the GAUSSIAN 98 programs, are supplemented with an additional set (*3s3p2d2f1g*) of bond functions, aug-cc-pVQZ+(*3s3p2d2f1g*).^{15,32} The set of bond functions are centered at the midpoint between the Ne and the Br_2 center of mass. All computations are carried out at the CCSD(T) level of theory, and in all calculations, *6d* and *10f* Cartesian functions are used.

The intermolecular energy between Ne and Br_2 is calculated using the supermolecular approach. The interaction energy, ΔE , is given as the difference between the total energy of the complex, E_{NeBr_2} , and the sum of the energies of the monomers, $E_{\text{Ne}} + E_{\text{Br}_2}$. The standard counterpoise method³³ is used for the correction of basis set superposition error (BSSE). The results of the CCSD(T) interaction energies for NeBr_2 are listed in Table I for the indicated values of r , R , and θ . We examine the interaction energies at five Br–Br distances around the equilibrium bond length of $2.281 \text{ \AA}$. The results are qualitatively similar. For all the r values the linear configuration is found to be lower in energy than the T-shaped one. When the Br–Br bond is lengthened the energy difference increases slightly but when the Br–Br bond

TABLE I. CCSD(T) interaction energies for the $\text{Ne}-\text{Br}_2$ molecule obtained with the aug-cc-pVQZ+(*3s3p2d2f1g*) basis set for the Ne and SDD+G(*3df*) ECP for Br for the indicated r , R , θ values.

$R \text{ (\AA)}$	$\Delta E \text{ (cm}^{-1}\text{)}$				
	$\theta=0^\circ$	$\theta=30^\circ$	$\theta=45^\circ$	$\theta=60^\circ$	$\theta=90^\circ$
$r=2.0998 \text{ \AA}$					
2.5	...	...	...	...	2153.5
3.0	...	...	...	...	144.83
3.25	...	...	...	...	-42.84
3.5	...	...	...	197.88	-87.94
3.75	406.93	388.80	190.72	16.83	-84.14
4.0	17.73	65.86	13.56	-39.68	-67.55
4.5	-89.72	-56.07	-47.67	-43.45	-37.11
5.0	-53.57	-40.34	-32.46	-25.96	-19.68
7.0	-4.43	-3.93	-3.40	-2.87	-2.30
9.0	-0.79	-0.79	-0.63	-0.57	-0.50
$r=2.1733 \text{ \AA}$					
2.5	...	...	...	...	2097.25
3.0	...	...	...	...	146.43
3.25	...	...	...	...	-39.61
3.5	...	...	...	189.16	-85.59
3.75	498.71	447.0	211.86	20.54	-82.83
4.0	44.64	85.39	20.13	-38.84	-66.96
4.5	-91.83	-56.18	-48.20	-43.98	-37.09
5.0	-56.40	-41.78	-33.30	-26.38	-19.75
7.0	-4.63	-4.06	-3.51	-2.91	-2.34
9.0	-0.81	-0.72	-0.63	-0.57	-0.50
$r=2.281 \text{ \AA}$					
2.5	...	...	...	...	1998.34
3.0	...	...	...	...	144.56
3.25	...	...	...	...	-36.75
3.5	...	...	...	224.04	-82.85
3.75	664.08	546.79	246.84	26.42	-81.10
4.0	96.02	120.18	32.15	-37.28	-66.04
4.5	-93.78	-55.46	-48.60	-44.62	-36.98
5.0	-60.66	-43.91	-34.54	-26.95	-19.81
7.0	-4.96	-4.28	-3.62	-2.98	-2.37
9.0	-0.83	-0.77	-0.68	-0.60	-0.52
$r=2.3887 \text{ \AA}$					
2.5	...	...	...	...	1884.28
3.0	...	...	...	...	138.51
3.25	...	...	...	...	-35.73
3.5	...	...	...	239.86	-80.81
3.75	875.04	666.01	286.50	32.72	-79.56
4.0	165.50	163.37	46.20	-35.38	-65.14
4.5	-93.65	-53.46	-48.60	-45.08	-36.78
5.0	-64.98	-45.98	-35.73	-27.52	-19.84
7.0	-5.26	-4.47	-3.75	-3.05	-2.39
9.0	-0.85	-0.79	-0.68	-0.60	-0.52
$r=2.4622 \text{ \AA}$					
2.5	...	...	...	...	1800.06
3.0	...	...	...	...	132.38
3.25	...	...	...	...	-35.90
3.5	...	...	...	250.59	-79.73
3.75	1051.21	759.73	316.26	37.22	-78.61
4.0	225.92	198.36	57.17	-33.90	-64.52
4.5	-91.87	-51.20	-48.30	-45.34	-36.60
5.0	-67.90	-47.30	-36.50	-27.85	-19.80
7.0	-5.50	-4.63	-3.82	-3.09	-2.41
9.0	-0.92	-0.81	-0.72	-0.59	-0.52

is shortened the energy difference decreases. We should note that the interaction energies of T-shaped structures are found to be more sensitive to small changes of the Br–Br bond length than for linear configurations.

TABLE II. Parameters for the $V(R, \theta_i; r_k), i, k = 1-5$ potential, [Eq. (2)] for NeBr₂ complex. Distances are in Å and energies in cm⁻¹. Figures in parentheses are powers of 10.

$r = 2.0998 \text{ Å}$					
θ_i	α_0^{i1}	α_1^{i1}	α_2^{i1}	α_3^{i1}	α_4^{i1}
0°	102.419	1.932 8	4.310 57	661 108	-1.390 93(07)
30°	117.415	1.814 51	4.217 5	720 854	-2.174 24(07)
45°	77.426 7	1.761 75	4.197 32	540 647	-1.373 53(07)
60°	7.340 29	1.684 91	4.767 01	238 968	1.640 34(06)
90°	0.309 456	1.720 61	5.313 54	179 569	3.039 95(06)
$r = 2.1733 \text{ Å}$					
θ_i	α_0^{i2}	α_1^{i2}	α_2^{i2}	α_3^{i2}	α_4^{i2}
0°	125.783	1.923 5	4.290 19	747 739	-1.852 58(07)
30°	130.403	1.807 64	4.216 28	758 363	-2.431 86(07)
45°	82.558 2	1.762 31	4.196 13	566 055	-1.486 29(07)
60°	7.355 96	1.535 78	4.969 11	-6427.52	7.750 77(06)
90°	4.297 45	1.694 74	4.544 56	173 437	2.001 3(06)
$r = 2.281 \text{ Å}$					
θ_i	α_0^{i3}	α_1^{i3}	α_2^{i3}	α_3^{i3}	α_4^{i3}
0°	185.805	1.907 64	4.234 92	944 031	-2.968 02(07)
30°	202.883	1.801 3	4.119 38	941 604	-3.547 07(07)
45°	158.711	1.7590 1	4.004 76	707 064	-2.381 9(07)
60°	14.879 3	1.672 95	4.568 85	265 385	-327 985
90°	1.835 84	1.681 27	4.817 68	185 430	2.306 98(06)
$r = 2.3887 \text{ Å}$					
θ_i	α_0^{i4}	α_1^{i4}	α_2^{i4}	α_3^{i4}	α_4^{i4}
0°	268.448	1.889 77	4.184 98	1.183 93(06)	-4.429 92(07)
30°	274.954	1.7913 8	4.065 63	1.105 51(06)	-4.613 12(07)
45°	202.364	1.752 37	3.950 5	784 113	-2.874 21(07)
60°	7.154 44	1.654 01	4.841 71	226 658	2.493 13(06)
90°	0.485 259	1.669 81	5.232 88	198 889	2.550 62(06)
$r = 2.4622 \text{ Å}$					
θ_i	α_0^{i5}	α_1^{i5}	α_2^{i5}	α_3^{i5}	α_4^{i5}
0°	355.329	1.877 41	4.140 55	1.422 23(06)	-5.872(07)
30°	362.746	1.785 13	4.003 71	1.276 38(06)	-5.719 04(07)
45°	34.148 9	1.717 79	4.583 65	423 381	-6.091 59(06)
60°	8.122 94	1.644 92	4.817 36	225 462	2.345 77(06)
90°	0.702 801	1.657 3	5.129 01	201 821	2.353 48(06)

III. DYNAMICAL CALCULATIONS

A. Potential energy surface

In order to represent the potential energy surface for the NeBr₂ complex we used an analytical functional form to fit the CCSD(T) *ab initio* data. We used an expansion in Legendre polynomials, $P_\lambda(\cos \theta)$, to describe the two-dimensional Ne . . . Br₂ interaction potential,

$$V(R, \theta; r_k) = \sum_{\lambda} V_{k\lambda}(R) P_\lambda(\cos \theta), \quad k = 1-5, \quad (1)$$

with $\lambda = 0, 2, 4, 6, 8$ due to the symmetry of the system with respect to $\theta = 90^\circ$. The $V_{k\lambda}(R)$ coefficients are obtained by a collocation method applying the following procedure. For each of the five values of angle θ , we fitted the CCSD(T) data to a Morse-vdW function,

$$V(R, \theta_i; r_k) = \alpha_0^{ik} (\exp(-2\alpha_1^{ik}(R - \alpha_2^{ik})) - 2 \exp(-\alpha_1^{ik}(R - \alpha_2^{ik}))) - \frac{\alpha_3^{ik}}{R^6} - \frac{\alpha_4^{ik}}{R^8}, \quad (2)$$

with parameters α_0^{ik} , α_1^{ik} , α_2^{ik} , α_3^{ik} and α_4^{ik} , where i and $k = 1-5$. The resulting parameters listed in Table II are obtained using a nonlinear least-squares fitting to the *ab initio* points. The model potential reproduces very well the *ab initio* values with a maximum standard deviation of 0.67 cm⁻¹ for all calculated values.

Figure 1 presents a two-dimensional contour plot of the $V(R, \theta; r_e = 2.281 \text{ Å})$ surface in Cartesian coordinates. The equipotential curves are shown for Ne moving around of Br₂ molecule with fixed r_e bond length. The NeBr₂ potential energy surface exhibits two minima. The global minimum with an energy of -95.14 cm⁻¹ at $R = 4.48 \text{ Å}$ and $\theta = 0^\circ$, corresponds to a linear configuration. The second minimum,

FIG. 1. Contour plots of the NeBr₂ potential energy surface, $V(R, \theta)$ [Eq. (3)]. Contour intervals are of 15 cm⁻¹ and for energies from -90 to 15 cm⁻¹. The Br-Br bond length is fixed at 2.281 Å.

with energy of -86.11 cm⁻¹, is at $R = 3.6$ Å and $\theta = 90^\circ$, corresponds to a T-shaped configuration of the complex. The potential in the neighborhood of the linear well is more rigid than near the T-shaped configuration. The isomerization barrier between the two wells is at energy of ~ -44.5 cm⁻¹ (50.6 cm⁻¹ above the global linear minimum), which is high enough to expect the lowest vibrational levels of these complexes to be localized in either the linear or T-shaped well.

B. Vibrational predissociation calculations of NeBr₂ ($X, v=1$)

The method we use has been previously described^{34,35} and will only be briefly presented here. The rovibrational Hamiltonian in the Jacobi coordinate system has the form

$$\hat{H} = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial R^2} + \frac{\hat{j}^2}{2\mu_2 r^2} + \frac{\hat{l}^2}{2\mu_1 R^2} + V(R, \theta, r) + \hat{H}_{\text{Br}_2}, \quad (3)$$

where $\hat{H}_{\text{Br}_2} = -(\hbar^2/2\mu_2)(\partial^2/\partial r^2) + V_{\text{Br}_2}(r)$ is the vibrational Hamiltonian for a free Br₂ molecule. $\mu_1^{-1} = m_{\text{Ne}}^{-1} + (2m_{\text{Br}})^{-1}$ and $\mu_2^{-1} = m_{\text{Br}}^{-1} + m_{\text{Br}}^{-1}$ are the reduced masses, m_{Ne} and m_{Br} are the atomic masses, $\hat{l}$ and $\hat{j}$ are the angular momenta operators associated with the vectors $\mathbf{R}$ and $\mathbf{r}$, respectively, leading to a total angular momenta $\hat{J} = \hat{l} + \hat{j}$. Here all calculations are performed for $J=0$. $V(R, \theta, r)$ is the intermolecular vdW potential given by the Eq. (1) and $V_{\text{Br}_2}(r)$ is the one-dimensional Br₂ ground state potential function. The eigenvalues and eigenfunctions of diatomic $\hat{H}_{\text{Br}_2}$ Hamiltonian are denoted $E_{\text{Br}_2}(v)$ and $\chi_v(r)$, respectively, and are evaluated by solving the one-dimensional (1D) Schrödinger equation using a combined Truhlar-Numerov algorithm.³⁶

The vibrational predissociation (VP) of the vdW complex implies the flowing of energy from the diatomic vibration toward the vdW bond, giving rise to its breaking up. Due to the large mismatch of the frequencies corresponding to the diatomic and vdW vibrations, the VP process can be described within a diabatic approximation. Therefore, in a zero-order description, a discrete state corresponding to an excited level of the diatomic moiety (v_i) is faced to the continuum of a lower level ($v_f < v_i$). Such discrete states are written as

$$|\Phi_{v_i}^d(R, \theta, r)\rangle = \phi^d(R, \theta) |\chi_{v_i}(r)\rangle, \quad (4)$$

where ϕ^d is a discrete eigenfunction of the Hamiltonian [Eq. (3)] averaged over the diatomic vibrational coordinate,

$$H_{v_i} \phi^d = E \phi^d, \quad (5)$$

with H_v being

$$H_v = \langle \chi_v | H | \chi_v \rangle = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial R^2} + \frac{l^2}{2\mu_1 R^2} + V_{v,v}(R, \theta) + E_{\text{Br}_2}(v) + \frac{B_v j^2}{\hbar^2}, \quad (6)$$

where $v = v_i$ or v_f , $V_{v,v}(R, \theta) = \langle \chi_v | V(R, \theta, r) | \chi_v \rangle$ is the intermolecular vdW potential of NeBr₂ averaged over the Br₂ v vibrational eigenfunction and B_v is the Br₂ average rotational constant.

In turn, the relevant continuum states can be expressed as

$$|\Phi_{v_f j_f}^\epsilon(R, \theta, r)\rangle = \phi_{v_f j_f}^\epsilon(R, \theta) |\chi_{v_f}(r)\rangle. \quad (7)$$

The ϕ^ϵ are continuum solutions at an energy ϵ of the Schrödinger equation

$$H_{v_f} \phi_{v_f j_f}^\epsilon = \epsilon \phi_{v_f j_f}^\epsilon \quad (8)$$

with H_{v_f} given by the expression of Eq. (6).

In the Golden rule approximation,³⁴ the partial halfwidth associated with the vibrational predissociation of an initial state $|\phi_{v_i}^d\rangle$ into a final continuum state $|\phi_{v_f j_f}^E\rangle$ is given by

$$\Gamma_{j_f} = \pi |\langle \phi_{v_i}^d | V_{v_i v_f} | \phi_{v_f j_f}^E \rangle|^2, \quad (9)$$

where $|\phi_{v_f j_f}^E\rangle$ are obtained through a close-coupling calculation in the (R, θ) variables³⁴ and evaluated at the same energy E as the discrete state. $V_{v_i v_f} = \langle \chi_{v_i} | V(R, \theta, r) | \chi_{v_f} \rangle$ is the coupling of an initial Br₂ v_i vibrational state with a final v_f state and is given by the off-diagonal terms of the interaction $V(r, R, \theta)$ potential. The halfwidth of the initial state is $\Gamma = \sum_{j_f} \Gamma_{j_f}$ and the associated lifetime for vibrational predissociation is given by $\tau = \hbar/2\Gamma$. Final rotational state distributions for the diatomic fragments can be calculated as, $P_j = \Gamma_{j_f}/\Gamma$.

In line-shape-like calculations the total fragmentation cross section, as a function of the energy, is written as

$$\sigma(E) = \sum_j \sigma_j(E) \quad (10)$$

with

$$\sigma_j(E) = |\langle \Phi_{v_i}^d | \Phi_{v_f j_f}^E \rangle|^2 \quad (11)$$

being the partial cross section for the excitation of an initial bound state of the complex at the v_i level of the diatom to a final continuum state at E energy. $\Phi_{v_f j_f}^E$ results from close-coupling calculations in all (R, θ, r) variables.³⁵ Finally, the rotational distribution of the diatomic fragments is given by

$$P_j(E_0) = \frac{\sigma_j(E_0)}{\sigma(E_0)}. \quad (12)$$

E_0 is the energy position of the resonance in the line shape calculations, corresponding to the maximum of the $\sigma(E)$ profile.

C. Results

The vibrational predissociation process of interest is

where v_i , v_f are the vibrational quantum numbers corresponding to Br₂ stretch mode and n to vibrational vdW modes. Here we performed calculations for $v_i=1$ and $v_f=0$ with $n=0,1$.

First, we calculate the ground ($v_f=0$) and the first excited ($v_i=1$) states of the Br₂ diatom, using cubic-spline interpolation to CCSD(T) *ab initio* data²⁷ to reproduce the V_{Br_2} potential at any r point.

Starting from the $V(R, \theta; r_k)$ potential of Eq. (1), 1D cubic-spline interpolation is used to compute the value of $V(R, \theta, r)$ at eleven Gauss–Legendre points in the interval of $2.081 < r < 2.481$ Å. In this way, the $V_{v_i v_f}$ potential matrix elements are calculated using Gaussian quadrature. The discrete ϕ^d states are obtained by diagonalizing the Hamiltonian of Eq. (6) for $v_i=1$. The Hamiltonian is represented on a finite two-dimensional basis set. For the angular coordinate we used orthonormalized Legendre polynomials $\{P_j(\cos \theta)\}$ as basis functions, with $j=0, 2, \dots, 54$. For the radial R coordinate, numerical $\{f_n(R)\}$ basis functions are obtained by solving the 1D Schrödinger equation using the potentials given by Eq. (2). For θ values of 0° and 90° , we choose $\{f_n(R)\}_{n=1-8}$ basis functions orthonormalized by a Gram–Schmidt procedure.

The results for the NeBr₂(X) potential show that the lowest two vdW vibrational levels ($n=0,1$) are at energies of -67.892 and -62.860 cm⁻¹ and the associated wave functions correspond to linear and T-shaped configurations, respectively. Once the wave functions for the discrete and continuum states of NeBr₂ complex have been calculated, the vibrational predissociation dynamics is described using Golden rule and line shape approaches. The Golden rule calculations estimate a vibrational predissociation lifetime for the ground vdW state of 0.49 μs ($\Gamma = 5.44 \times 10^{-6}$ cm⁻¹) and 0.9 μs ($\Gamma = 2.95 \times 10^{-6}$ cm⁻¹) for the first excited vdW state. The resonances are found at energies of -67.8918 and -62.8599 cm⁻¹, respectively.

For such narrow resonances (of the order of 10^{-6} cm⁻¹) and to refine the Golden rule resonance positions (E_0) we evaluate the total cross section $\sigma(E)$ at several energies around E_0 through the above mentioned close-coupling scheme.³⁵ In Fig. 2 we present the calculated $\sigma(E)$ as a function of the energy for the linear and T-shaped initial states. A Lorentzian fit to the $\sigma(E)$ gives halfwidth values of 6.08×10^{-6} cm⁻¹ (linear) and 3.53×10^{-6} cm⁻¹ (T-shaped). The corresponding lifetimes for vibrational predissociation become $\tau=0.44$ and 0.75 μs, respectively and the resonance positions are -67.8818 cm⁻¹ and -62.8570 cm⁻¹, respec-

FIG. 2. Lorentzian fit of $\sigma(E)$ in the energy region of the ($X, v=1$) resonance for the linear and T-shaped isomers of NeBr₂. The zeros of energy are at -67.8818 and -62.8570 cm⁻¹ for the linear and T-shaped levels, respectively.

tively. We should note that the energy of the ground $n=0$ level is close to the upper bound of the experimental estimation of the NeBr₂(X) dissociation energy $D_0 = 70.5 \pm 2.0$ cm⁻¹.³⁷ A previous theoretical study³⁸ using a semiempirical pairwise potential surface for NeBr₂(X) and the Golden rule approximation have predicted a lifetime of 5.9 μs. However, these calculations used an infinite order sudden (IOS) angular approximation, in addition to the diabatic vibrational approximation fully justified here.

Experimental measurements of the VP lifetime²² based on the ratio of the populations of NeBr₂ ($X, v=1$) to Br₂ ($X, v=1$) as a function of the distance from the nozzle have given a value of 8 ± 3 μs for the vibrational predissociation lifetime of NeBr₂ ($X, v=1$). In case that the NeBr₂ ($X, v=1$) lifetime is estimated²² from comparison of the intensity ratio of

$$\frac{I(\text{Br}_2(X, v=0))}{I(\text{NeBr}_2(X, v=0))}$$

to the intensity ratio of

$$\frac{I(\text{Br}_2(X, v=1))}{I(\text{NeBr}_2(X, v=1))}$$

for the smallest distance studied, a value of ≈ 1 μs has been obtained. Additionally, by extrapolation of lifetimes of vibrational levels in the B electronic state a value of 0.6 μs has also been mentioned.²² Given the difficulties of the experimental studies reported by Janda and co-workers²² the determination of the NeBr₂ ($X, v=1$) lifetime “should be regarded within an order of magnitude of the experimental 8 ± 3 μs value.”

Comparing Golden rule and line shape calculations, it can be seen that both approaches yield almost identical results for halfwidths of the resonances, with Golden rule halfwidths to lie slightly below the line shape ones. Concerning the energy positions of the above-mentioned resonances, line

FIG. 3. Decomposition of the initial wave function in terms of free rotor states (solid line) and final (dashed line) rotational distributions resulting for the vibrational predissociation of $(X, n, v=1)$, for $n=0$ (linear) and $n=1$ (T-shaped) levels of NeBr_2 , calculated using the CCSD(T) *ab initio* PES. In the inset, the initial (solid line) and final (dashed line) rotational distributions for the vibrational predissociation of $(X, n=0, v=1)$ level of NeBr_2 , calculated using empirical pairwise PES (Ref. 38).

shape calculations shift E_0 to lower values than the golden rule by 0.01 and 0.003 cm^{-1} , respectively. We should note that the estimated energy shifts are three to four orders of magnitude higher than the corresponding halfwidths. In both, Golden rule and line shape calculations the lifetime for the T-shaped resonance is longer (almost twice) than for the linear one according to the energy gap law.³⁹

Computed initial (decomposition of the initial wave function in terms of free rotor states) and final state rotational distributions of Br_2 subunit resulting from vibrational predissociation of the ground and the first excited vdW NeBr_2 ($X, v=1$) levels are shown in Fig. 3. The initial and final rotational distributions for the ground (linear) vdW state are similar to each other with a maximum at low values of j , approximately at $j=4$. This result is in excellent accord with experimental findings,²² where the energy transfer to rotation was not found to be important in the VP process on the ground electronic state of NeBr_2 . On the contrary, the initial and final rotational state distributions for the first excited (T-shaped) vdW state are totally different from each other. The final rotational distribution appears to be smooth and bimodal, with two broad peaks located around $j=2$ and $j=22$, which in turn presents a population about two times higher than that corresponding to $j=2$. Such kind of structures have been previously found both in experimental and theoretical studies on HeCl_2 ⁴⁰ and theoretical studies of HeICl ,⁴¹ NeICl ,³⁴ and HeBr_2 ⁴² in excited electronic states. The bimodal structure can be explained in terms of rotational rainbow effect⁴³ and is of course a clear manifestation of a quantum interference.⁴¹ In the case of NeBr_2 ($X, n=1$,

$v=1$), like in NeICl(B) , high j 's are predominantly populated, in contrast to the $\text{HeCl}_2(\text{B})$ case, where the main peak appears at low j values.

The VP rotational distributions of the NeBr_2 ($X, v=1$) complex are also calculated, within the Golden rule approach, using the semiempirical pairwise PES from Ref. 38. This PES has single T-shaped minimum with a depth of 92.0 cm^{-1} . The two lowest vdW levels, ground $n=0$ and bending excited $n=1$, are at energies of -70.98 and 52.30 cm^{-1} , respectively. Initial and final rotational state distributions calculated for the $n=0$ level are shown in the inset of Fig. 3(b). It should be noted that for the lowest T-shaped levels ($n=1$ for *ab initio* and $n=0$ for pairwise PES) initial distributions are almost identical [see Fig. 3(b)]. In both cases final distributions have a bimodal structure, but the magnitude of low- and high- j peaks is reversed. It is evident that the final rotational state distribution for VP of the linear isomer is determined by structure of initial wave function and is not affected by rotational energy transfer in VP processes, while for the T-shaped isomer the factor determining the final rotational distributions is the energy transfer to rotations. It should be concluded that the VP of both linear and T-shaped isomers proceeds through vibration-to-translation energy transfer with a contribution of vibration-to-rotation transfer in the latter case. While such a mechanism is typical for other T-shaped rare gas-dihalogen complexes, the behavior of their linear isomers is in contrast to the linear heavy atom-light diatom complexes like ArHF , where VP proceeds through vibration-to-rotation energy transfer assisted by strong and sharp interaction anisotropy.^{44,45}

The difference between the final state rotational distributions of Br_2 from the lowest two vdW levels of NeBr_2 ($X, v=1$) is crucial in determining the initial geometry of the complex. Unfortunately, no direct experimental measurements of the product state distribution on the ground NeBr_2 surface have been reported. However, Janda and co-workers²² have concluded that the energy transfer to rotation is not important in the vibrational predissociation process on the ground NeBr_2 state; that is in accord with the rotational state distribution obtained here for the linear vdW state for the complex. Final state rotational distributions are thus closely related to the topology of the ground electronic potential surface and suggest a possible experimental detection of linear and T-shaped isomers for the $\text{NeBr}_2(X)$ complex.

IV. CONCLUSIONS

The vibrational predissociation lifetime of NeBr_2 ($X, v=1$) in the ground electronic state with one vibrational quantum in the Br_2 stretch mode is calculated using high-level *ab initio* ground-state PES. The CCSD(T) surface has a double minimum topology and the two lowest vibrational vdW levels ($n=0,1$) for $J=0$ correspond to linear and T-shaped configurations.

Lifetimes are calculated using Golden rule approximation and full 3D line shape calculations. We found that the lifetime of the T-shaped resonance is longer (almost twice) than the one of the ground (linear) state. Lifetimes for NeBr_2

($X, v=1$) reported by experiment range from 0.6 to 8 ± 3 μ s. The present results are very close to the lower experimental estimate.

Further, final state rotational distributions for the $n=0$ and 1 vdW levels are computed and analyzed. It is shown that their structure provides information on the topology of the ground state potential. After comparing the theoretical rotational distributions for the linear/T-shaped isomers, and taking into account that a cold distribution has been experimentally suggested,²² we may speculate that the linear isomer of NeBr₂(X) was the one accessed by the experiment. In this context, it would be of great interest to obtain experimentally such distribution in order to justify our assertion.

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