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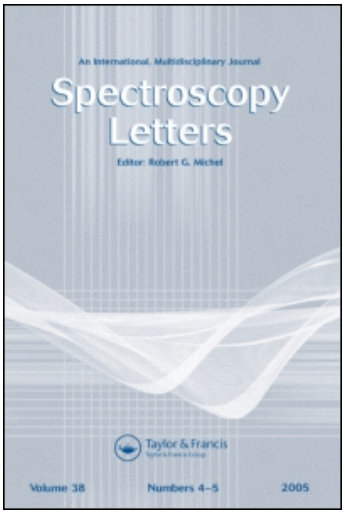

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APPROXIMATE QUANTAL CALCULATIONS ON THE PREDISSOCIATIVE LIFETIMES OF THE Ne...$Hal_2(X,v)$ (Hal = Cl,Br,I) VAN DER WAALS COMPLEXES

Key words: Vibrational predissociation, van der Waals complexes.

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Abstract

Predissociative lifetimes of several ground-state neon-halogene van der Waals complexes are calculated by the simple two-dimensional model and empirical potential energy surfaces. A reasonable agreement with the experimental lifetime is found for Ne...Br_2 complex and the vibrational predissociation rates of Ne...Cl_2 and Ne...I_2 complexes are predicted.

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I. INTRODUCTION

Vibrational predissociation (VP) of the van der Waals (vdW) complexes composed of the rare-gas atoms and halogene molecules were extensively studied since the pioneering works by Levy and co-workers[1,2]. Experimental techniques based on an excitation of the $X \rightarrow B$ transition in the halogene fragment provided detailed information on the lifetimes of B-state vibrational levels of the complexes (see for a review Refs. 3,4). Such measurements stimulated theoretical investigations on the VP dynamics of electronically excited complexes. Among the methods applied to calculations of predissociative linewidths much attention was paid to the three-dimensional Fermi Golden Rule (FGR) approaches combined with different approximations to the initial (bound) and final (scattered) wavefunctions. In this framework there was reached a good agreement with spectroscopic data for several complexes such as He...Cl_2[5], Ne...Cl_2[6,7] and others.

However, much less is known about VP of the ground-state complexes in spite of their importance in energy transfer processes, spectroscopy of the halogene molecules seeded in rare gas jets, transport properties of the gas mixtures and so on. It rises from the experimental difficulties in an accessment of the ground state vibrational levels[8]. To our knowledge, the

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direct experiments which aimed to obtain lifetimes of the ground state vibrational levels were performed only for $Ne...Br_2(X, v=1)$[8]. Some lower limits of the $Ne...Cl_2(X, v=1, 2)$ lifetimes were also estimated from the B-state spectroscopy[9].

In this letter we present preliminary results on the predissociative lifetimes to the $Ne...Hal_2(X, v)$ (Hal = ^{35}Cl, ^{79}Br, ^{127}I) complexes obtained within a simple two-dimensional FGR adiabatic model. Intermolecular potentials appropriate for these calculations were constructed with the help of literature data.

The next section contains the theoretical model formulation. In section III the potential evaluation and final results are described.

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II. THEORY

We consider two-degrees-of-freedom Hamiltonian for the experimental T-shaped (C_{2v}) geometry of $Ne...Hal_2$ complexes. The Ne motion relative to the Hal_2 center-of-mass is restricted within the vector $\hat{R}$ perpendicular to the Hal axis $\hat{r}$,

$$H = -\frac{1}{2m}\frac{\partial^2}{\partial r^2} - \frac{1}{2\mu}\frac{\partial^2}{\partial R^2} + U(r,R), \qquad (1)$$

where m and μ are corresponding reduced masses. The total potential is assumed to be a sum of atom-atom interactions,

$$U(r,R) = U_r(r) + U_{\mathcal{R}}(\mathcal{R}_1) + U_{\mathcal{R}}(\mathcal{R}_2), \quad (2)$$

and $\mathcal{R}_1$, $\mathcal{R}_2$ indicates the Ne-Hal distances. By symmetry, $\mathcal{R}_1$ and $\mathcal{R}_2$ are equal to each other and to

$$\mathcal{R} = (R^2 + 1/4r^2)^{1/2}. \quad (3)$$

This relation induces coupling of the $\hat{r}$ and $\hat{R}$ motions in the total potential

$$U(r,R) = U_r(r) + 2U_{\mathcal{R}}[\mathcal{R}(r,R)]. \quad (4)$$

The large mismatch of velocities (frequencies) in vibrations along $\hat{R}$ and $\hat{r}$ allows to use the adiabatic approximation, i.e. to represent a total wavefunction in the form

$$\Psi = \psi(r) \cdot \phi(R), \quad (5)$$

where ψ and ϕ are eigenvectors of the appropriate unperturbed Hamiltonian H_0:

$$H_0 = h_r + h_R$$

$$= \left(-\frac{1}{2m}\frac{\partial^2}{\partial r^2} + U_r(r) \right) + \left(-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} + U_R(R) \right). \quad (6)$$

In what follows we set U_R equal to $2U_{\mathcal{R}}(\bar{r},R)$; hereafter upper dash indicates an equilibrium value.

Thus, for the initial quasibound state of the complex one has

$$\Psi_{vn} = \psi_v(r) \cdot \phi_n(R) \quad (7)$$

$$h_r\psi_v(r) = E_v\psi_v(r) \quad (8)$$

$$h_R\phi_n(R) = E_n\phi_n(R), \quad (9)$$

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where v, n are vibrational quantum numbers for the Hal_2 and vdW stretching motions, respectively.

A final wavefunction for the particular decay channel v' ($v' < v$) is

$$\Psi_{v',\varepsilon} = \psi_{v'}(r) \cdot \phi_{\varepsilon}(R), \qquad (10)$$

where ϕ_{ε} is an unbound solution of the Schrödinger equation (9) for h_R at the energy $\varepsilon = E_v + E_n - E_{v'}$. The corresponding partial linewidth is then evaluated within Fermi Golden Rule approximation,

$$\Gamma_{vv'} = \pi \left|\langle \Psi_{v',\varepsilon} \right| V \left| \Psi_{vn} \rangle\right|^2, \qquad (11)$$

where V is a perturbation

$$V = H - H_0 = 2U_{\mathcal{R}}(r,R) - 2U_{\mathcal{R}}(\bar{r},R) \qquad (12)$$

Finally, the total linewidth is equal to

$$\Gamma_v = \sum_{v'=0}^{v-1} \Gamma_{vv'} \qquad (13)$$

The approach formulated above may be considered as a numerical version of the early analytical model proposed by Beswick and Jortner for linear complexes[10]. Obviously, their correction on the product channel interaction could be also included straightforwardly. However, it seems to be of minor importance for the lower vibrational excitations considered here and has not been taken into account. From the other hand, our model is very close to those which were used for particular complex configurations with the fixed $(\hat{r},\hat{R})$

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angle in a framework of the adiabatic infinite order sudden approximations to three dimensional dynamics[11].

We have solved one-dimensional Schrödinger equations using Numerov algorithm and evaluated two dimensional integrals (11) by modified Simpson 1/3 rule.

III. RESULTS

Potentials

For halogen fragments the RKR potential curves of the $X^1\Sigma_g^+$ state of the halogene molecules were used fragment. In order to obtain a simple functional form which is easily parameterized with experimental data the Ne-Hal interaction was assumed as a Morse potential including the parameters D, α and $\bar{R}$. To convert the spectroscopic constants to the atom-atom potential parameters we have used a simple procedure. Expanding $2U_{\mathcal{R}}(r,R)$ in Taylor series in R and r near the equilibrium and keeping only r-independent terms one obtains zeroth-order potential function $U_R^0(R)$ which has a Morse form with the parameters[12]

$$D_R = 2D, \quad \alpha_R = \alpha\, \bar{r}/\bar{R}, \quad \bar{R} = (\bar{R}^2 - 1/4\bar{r}^2)^{1/2} \qquad (14)$$

For vdW stretching vibrations these formulas relate the spectroscopic constants D_R, $\bar{R}$ and α_R (or $\omega_e\chi_e$) with the parameters of atom-atom interaction.

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TABLE 1

Ne - Hal Morse Atom-Atom Potential Parameters

Hal_2		D, cm^{-1}	α, $Å^{-1}$	$\bar{R}$, Å
Cl_2	I	36.75	1.71	4.22
	II	39.23	1.60	4.00
	III	35.435	1.92	3.52
Br_2	I	42.36	1.72	3.684
	II	47.33	1.60	4.179
I_2	I	42.5	1.49	4.51
	II	48.7	1.427	4.51

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Ne...Cl_2

$Cl_2(X)$ RKR potential is given in Ref.12.

The first set (I) of the atom-atom Morse potential parameters was extracted from the multiproperty fit of Ne...$Cl_2(X)$ interaction proposed by Reid et al.[14], while the second set (II) - from the Lennard-Jones potential of Secrest and Eastes[15]. However, we interpret it as a reference U_R^0 function in contrast to Ref.10, where it was considered as a pairwise interaction. Our interpretation seems to be more consistent with the averaged nature of this potential[16] and is supported by the similarity of the parameter sets I and II, see table 1.

TABLE 2

Predissociative Lifetimes of Ne...$Hal_2(X,v)$ Complexes, s

Hal_2	v	Potential[a]			Exptl.
		I	II	III	
Cl_2	1	$1.86\ 10^{-2}$	$1.61\ 10^{-1}$	$1.04\ 10^{-3}$	$> 10^{-5}$
	2	$7.73\ 10^{-3}$	$6.56\ 10^{-2}$	$4.42\ 10^{-4}$	$> 10^{-5}$
Br_2	1	$9.75\ 10^{-7}$	$2.46\ 10^{-6}$	—	$8\pm3\ 10^{-6}$
	2	$4.51\ 10^{-7}$	$1.12\ 10^{-6}$	—	—
I_2	1	$2.64\ 10^{-7}$	$2.82\ 10^{-7}$	—	—
	2	$1.32\ 10^{-7}$	$1.36\ 10^{-7}$	—	—

[a] See text for notation and table 1 for parameters.

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The calculated lifetimes for $v = 1$, 2 are given in table 2 together with their experimentally determined lower limits[9].

In addition, we have performed calculations with the third set of parameters (III) originated from the Ne...$Cl_2(B)$ potential energy surface of Halberstadt et al.[6] and consisting of the vdW Morse potential modified by anisotropic long-range terms. Three-dimensional calculations for Ne...$Cl_2(X)$ (only Cl_2 potential was changed relative to the B-state case) result in $9.0 \cdot 10^{-4}$ s lifetime value[6] which agrees with our estimate for the potential III given in table 2.

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Ne...Br_2

RKR potential $Br_2(X)$ is taken from Ref.17.

Two different vdW interactions have been considered. The first one (I) is constructed by with the help of experimental values of the X-state D_0 = 70.5 ± 2.0 cm^{-1}, Ref.18, and R_0 = 3.67 ± 0.01 Å [19] (subscript "0" indicates the ground vdW vibrational state). The α value has been approximated by that obtained from the Morse fit of the NeKr vibrational sequence[20]. A simple iterative procedure which utilize the formulas (13) as well as relations connecting the equilibrium values D and $\bar{R}$ with D_0 and R_0 allowed to determine the atom-atom potential parameters listed in table 1. A numerical value for D_0 = 70.68 cm^{-1} obtained with this potential indicates that the error of recalculation procedure is less than 0.2 cm^{-1}.

Potential II is those of Secrest and Eastes[15] implemented as described above for Ne...Cl_2.

In table 2 calculated lifetimes are presented with the abovementioned experimental estimate.

Ne...I_2

Ranges for the D_R and α_R values of Ne...$I_2(X)$ were experimentally determined by Blazy et al.[21]. These constants together with the $\bar{R}$ value from Secrest-Eastes potential define the set I of parameters, while the set

II corresponds again to Secrest and Eastes[15], see table 1. RKR curve of I_2 is taken from Ref.22.

To our knowledge, there is no experimental information on VP of Ne...$I_2(X)$, so only calculated lifetimes are presented in table 2.

IV. CONCLUSIONS

Restricted two-dimensional quantal model have been used in order to calculate lifetimes of the lowest vibrational levels in the ground electronic states of the vdW complexes formed by the Ne atom with Cl_2, Br_2 and I_2 molecules. Two different vdW potentials have been systematically tested in these calculations.

Less or more definite comparison with the experimental values is possible only for Ne...$Br_2(X, v=1)$. Both potentials give the order-of-magnitude estimates and indicate the validity of the theoretical model. However, predicted lifetimes should grow up within three-dimensional calculations[11] so that the more reliable "spectroscopic" potential I which gives some poorer agreement with the experimental data in our model could appear a better one within more accurate calculations.

The lack of experimental data for complexes with Cl_2 and I_2 does not allow to split inaccuracies of the theory and uncertainties of the potentials. We hope

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that for these systems the overall agreement is comparable with those achieved in bromine case. Comparison with more accurate theoretical results for the potential III of Ne...Cl_2 gives some proofs for this suggestion.

It should be also noted that the results obtained with the Secrest-Eastes interactions (II) provide a good picture of the qualitative trend of lifetimes in the Ne..Cl_2, Br_2 and I_2 series.

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