

Comment on vibrational predissociation of polyatomic van der Waals complexes

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Levy¹ has utilized the energy gap law (EGL) for vibrational predissociation (VP) of triatomic van der Waals molecules (VDWMs)² to discuss the short lifetime³ of the interesting polyatomic complex HeNO₂. He points out¹ that nonadiabatic interstate scrambling^{4,5} between the excited ²B₂ state and the ground ²A₁ state of NO₂ results in a level structure which is characterized by a relatively high density of vibronic levels (~0.05 cm), whereupon the effective energy gap between adjacent vibronic levels is considerably reduced. We would like to point out that such a qualitative application of the EGL for the VP of a complex consisting of a rare-gas atom X bound to a polyatomic molecule M, which is characterized by effective interstate mixing, requires the incorporation of anharmonicity effects. Consider a VDWM M-X which is characterized by the Hamiltonian for the internal motion $H = H_0 + V$ with $H_0 = H_M + H_{X,M}$, where H_M is the Hamiltonian for the conventional molecule M, $H_{X,M}$ denotes the (zero-order) X-M interaction and where X moves relative to the center of mass (c.m.) of M, which is frozen at its equilibrium nuclear configuration, and V corresponds to the residual interaction. The zero-order diabatic states of H_0 are $\mathbf{X}^M \phi_i(R_{X,M})$ and $\mathbf{X}^M \phi_e(R_{X,M})$, where \mathbf{X}^M is the nuclear wavefunction of M, while ϕ_i and ϕ_e correspond to bound and continuum states of the VDW bond, respectively. For the hypothetical case of a harmonic molecule $\mathbf{X}^M_{[v_j]} = \prod_j \chi_{v_j}(q_j)$, where $\chi_{v_j}(q_j)$ is the nuclear wavefunction for the j th normal mode, specified in terms of the normal coordinate q_j and the vibrational state v_j . On the basis of our numerical calculations for X-BC² as well as for BC-BC⁶ we assert that the dominant contribution to the perturbation Hamiltonian involves linear terms in the internal displacements X_β , $V(X_\beta, R_{c.m.}) = \sum_\beta X_\beta f_\beta(R_{X,M})$ so that for the harmonic molecule $V = \sum_j q_j g_\beta(R_{X,M})$, where f_β and g_β are some functions of the separation $R_{X,M}$ between X and the c.m. of M. It is evident that the discrete-continuum coupling for the harmonic molecule is determined by the selection rules $\Delta v_j = \pm 1$ for a single mode, while $\Delta v_k = 0$ for

$k \neq j$. This simple selection rule leads to a propensity rule for the VP process which essentially involves one quantum jump within a normal mode of the harmonic molecule. Thus, the VDWM consisting of a harmonic conventional molecule exhibits the EGL separately for each normal mode of M. The Levy hypothesis can be realized provided that anharmonicity effects are incorporated. One possible representation of the nuclear wavefunction of \mathbf{X}^M involves a harmonic basis

$$\mathbf{X}^M_\alpha = \sum_{v_1} \sum_{v_2} \cdots C_{v_1 v_2}^{(\alpha)} \cdots \chi_{v_1}(q_1) \chi_{v_2}(q_2) \cdots$$

These wavenumbers, together with the perturbation $[V(X_\beta, R_{X-M})]$, will result, obviously, in quantum jumps between close-lying nuclear states $X^M_\alpha \phi_i$ and $X^M_\alpha \phi_e$, the coupling being determined by the expansion coefficients $C_{v_1 v_2}^{(\alpha)}$ and $C_{v'_1 v'_2}^{(\alpha')}$. Obviously, this expansion for X^M_α is not unique, and alternative representation, e.g., in terms of the zero-order bond modes, seems promising. Thus, anharmonicity effects are crucial for the reduction of the effective energy gap in the VP of polyatomic VDWMs. These anharmonicity effects have interesting implications for the study of intramolecular vibrational energy exchange in a normal M molecule interrogated by monitoring the VP of the X-M complex.

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