

Scaling of mean lifetimes of metastable molecular states with angular-momentum and vibrational quantum numbers

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The dependence of the mean lifetimes of metastable molecular ions on the vibrational and rotational quantum numbers is determined empirically. From the mean lifetimes calculated using the phase-shift method for the ${}^3\text{He}^4\text{He}^{2+}$ and ${}^{20}\text{Ne}^{40}\text{Ar}^{2+}$ metastable molecular ions, we show that the mean lifetimes of rotational states decrease with angular momentum l approximately as $\tau_l \propto e^{-\alpha l(l+1)}$, and the mean lifetimes of vibrational states decrease with the vibrational quantum number v approximately as $\tau_v \propto e^{-\beta v}$. These empirical results are justified by using the Wentzel-Kramers-Brillouin approximation to estimate the analytic form of the scaling laws.

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In recent years there has been an increasing interest in the theoretical and experimental studies of metastable states of molecules and molecular ions. The potential curves of these states have a local minimum at small internuclear separation, R_0 , which is higher than the potential energy at the dissociation limit, thus they can dissociate by tunneling through the potential barrier. The tunneling rates of the different vibrational states are extremely sensitive to the shape of the potential curve $V(R)$ and the energy of the vibrational state E_v , as can be seen from the WKB formula [1]

$$\tau^{-1} = \lambda = f_v e^{-2 \sqrt{2\mu} \int_a^b dR \sqrt{V(R) - E_v}}, \quad (1)$$

where a and b are the classical turning points, f_v is the vibrational frequency, and μ is the reduced mass of the molecule.

Tunneling decay rates have been calculated using the WKB approximation, see, for example, [2-5]. Quantum mechanical calculations of the resonances' energies and widths have been performed only more recently. For example, Babb and Du used the amplitude method to calculate the mean lifetimes of ${}^3\text{He}^4\text{He}^{2+}$ [6], and Chen *et al.* [7] used the phase-shift method to calculate the mean lifetimes of ${}^{20}\text{Ne}^{40}\text{Ar}^{2+}$. These quantum mechanical calculations of the decay rates are rather time consuming because the states have very narrow widths [7].

Estimates of the mean lifetimes of some metastable molecular states have been inferred from experiments. For example, Belkacem *et al.* [8] reported a mean lifetime longer than 5 μsec for the ${}^3\text{He}^4\text{He}^{2+}$ molecular ion. Recently, direct measurements of the mean lifetime of ${}^{20}\text{Ne}^{40}\text{Ar}^{2+}$ have been reported by Ben-Itzhak *et al.* [9]. According to the calculations of Chen *et al.* [7] this measured value is close to the mean lifetime of the $v = 12$ vibrational level of the ground electronic state. Recent direct measurements of the dissociation of ${}^3\text{He}^4\text{He}^{2+}$ also indicated that this molecular ion might be in highly excited rotational states [10].

From our experience the search of the rotational and vibrational states which have proper mean lifetimes corresponding to the measured ones is rather time consuming if quantum mechanical methods are used. In this Brief Report we present the empirical formulas which give the dependence of the mean lifetimes on the vibrational and rotational quantum numbers (atomic units are

used throughout this paper). High precision mean lifetimes have been determined using the phase-shift method as described in our earlier work [7]. It will be shown that these mean lifetimes scale as

$$\tau_v \propto e^{-\beta v} \quad (2)$$

for the different vibrational states with the same l , and as

$$\tau_l \propto e^{-\alpha l(l+1)} \quad (3)$$

for the rotational states with the same v , where β and α are constants. These scaling laws were obtained initially empirically from the calculated values. In the following we used the WKB approximation to "justify" these relations.

The two molecular ions to be examined are ${}^3\text{He}^4\text{He}^{2+}$ and ${}^{20}\text{Ne}^{40}\text{Ar}^{2+}$, where the ground state potential curves have been calculated by Ackermann and Hogreve [3] and by Koch *et al.* [11], respectively. Both potential-energy curves for $l = 0$, shown as dotted curves in Fig. 1, have been used in our previous mean lifetime calculations for the different vibrational-rotational states. For states with angular momentum l , a centrifugal term was added, i.e., $V_l(R) = V_0(R) + l(l+1)/2\mu R^2$, where the $V_0(R)$ is the $l = 0$ potential-energy curve shown in Fig. 1.

To obtain the empirical formula, we carried out the WKB approximation by fitting the potential energy near the barrier with an inverted harmonic oscillator potential, namely,

$$V_{\text{model}}(R) \simeq U_l - a_l (R - R_b)^2, \quad (4)$$

where U_l and a_l are fitted parameters for each value of angular momentum l , and R_b is the location of the maximum of the barrier. As an example, the fitted potentials for $l = 0$ for the two systems, shown in solid lines in Fig. 1, are a reasonable approximation of the potential energy near the barrier maximum. However, far from the maximum the potential becomes asymmetric and the parabola given in Eq. (4) fails to fit the potential at large R values, as can be seen from Fig. 1(b). As our main interest was the general dependence of the mean lifetime of states close to the maximum of the potential barrier, where the fit is good, on the quantum numbers v and l , we have chosen the symmetric potential-energy barrier because it simplifies the WKB calculations so that the dependence of the mean lifetime on v and l can be

followed analytically.

Explicitly, the WKB phase integral for the v, l state yields

$$\begin{aligned} \int_a^b dR \sqrt{V_l(R) - E_{vl}} \\ = \int_a^b dR \sqrt{U_l - a_l(R - R_b)^2 - E_{vl}} \\ = \frac{\pi}{2} \frac{U_l - E_{vl}}{\sqrt{a_l}}, \end{aligned} \quad (5)$$

where the turning points for the model potential are equal to $R_b \pm \sqrt{(U_l - E_{vl})/a_l}$. Substituting Eq. (5) for the integral in Eq. (1) gives the mean lifetime

$$\tau_{vl} = f_v^{-1} e^{\pi \sqrt{\frac{2\mu}{a_l}} (U_l - E_{vl})}. \quad (6)$$

In Eq. (6), if the vibrational energy levels are approximated by the harmonic oscillator formula, i.e., $E_{vl} = \omega_l (v + \frac{1}{2})$, then

$$\tau_{vl} \propto e^{-\beta v}, \quad (7)$$

where $\beta = \pi \omega_l \sqrt{\frac{2\mu}{a_l}}$, and $\omega_l = \sqrt{k_l/\mu}$ (k_l is found by fitting a harmonic oscillator potential around R_0). In Eq. (7), we have neglected the dependence of the vibrational frequency f_v on the vibrational quantum number.

The validity of Eq. (7) is checked against the actual calculated values in Fig. 2 for the mean lifetimes of different vibrational states of ${}^3\text{He}^4\text{He}^{2+}$ and ${}^{20}\text{Ne}^{40}\text{Ar}^{2+}$. The results of using Eq. (7), with fitted parameters, are shown as solid lines. The curves represent the actually calculated mean lifetimes rather well except for the higher vibrational states of ${}^{20}\text{Ne}^{40}\text{Ar}^{2+}$. The mean lifetimes of highly excited vibrational states increasingly deviate from the model because their energy is not well approximated by the harmonic oscillator formula. Correction to the energy from the nonlinear $(v + \frac{1}{2})^2$ term contributes more than 20% of the energy for states with $v \geq 10$. Even such a deviation can cause a significant shift of the mean lifetimes away from Eq. (7). As another check, we found that the slope of the exponentials derived from the best fit to the phase-shift values shown in Fig. 2 yields $\beta_{fit} = 10.9 \pm 0.4$ for ${}^3\text{He}^4\text{He}^{2+}$ which is in reasonable agreement with the $\beta_{model} = 12.43$ value predicted by the simple model. Similar agreement was found for ${}^{20}\text{Ne}^{40}\text{Ar}^{2+}$, i.e., $\beta_{fit} = 13.4 \pm 0.2$ while $\beta_{model} = 11.0$.

Next we consider the dependence of the mean lifetimes on the rotational angular-momentum quantum number. The effective potential for states with angular momentum l is given by $V_l(R) = V_0(R) + l(l+1)/2\mu R^2$, where $V_0(R)$ is the potential-energy curve for $l=0$ (see Fig. 1). This potential-energy curve is approximated around the maximum of the barrier by a parabolic barrier of the form given in Eq. (4). The fitting parameters U_l and a_l can be written as a function of the fitting parameters U_0 and a_0 for the $V_0(R)$ potential (i.e., the $l=0$ case) as follows:

$$\begin{aligned} V_l(R) &= U_0 - a_0 x^2 + \frac{l(l+1)}{2\mu R_b^2} \frac{1}{(1 + \frac{x}{R_b})^2} \\ &= U_0 - a_0 x^2 \\ &\quad + \frac{l(l+1)}{2\mu R_b^2} \left[1 - 2\frac{x}{R_b} + 3\left(\frac{x}{R_b}\right)^2 \right. \\ &\quad \left. - 4\left(\frac{x}{R_b}\right)^3 + O(4) \right], \end{aligned} \quad (8)$$

where $x = R - R_b$ and the centrifugal potential was expanded for $x/R_b \ll 1$. Keeping terms up to $(\frac{x}{R_b})^2$ one gets

$$\begin{aligned} V_l(R) &= U_0 + \frac{l(l+1)}{2\mu R_b^2} + \frac{1}{4} a_0 \left(1 - \frac{3l(l+1)}{2\mu a_0 R_b^4} \right) c^2 \\ &\quad - a_0 \left(1 - \frac{3l(l+1)}{2\mu a_0 R_b^4} \right) x_l^2 = U_l - a_l x_l^2, \end{aligned} \quad (9)$$

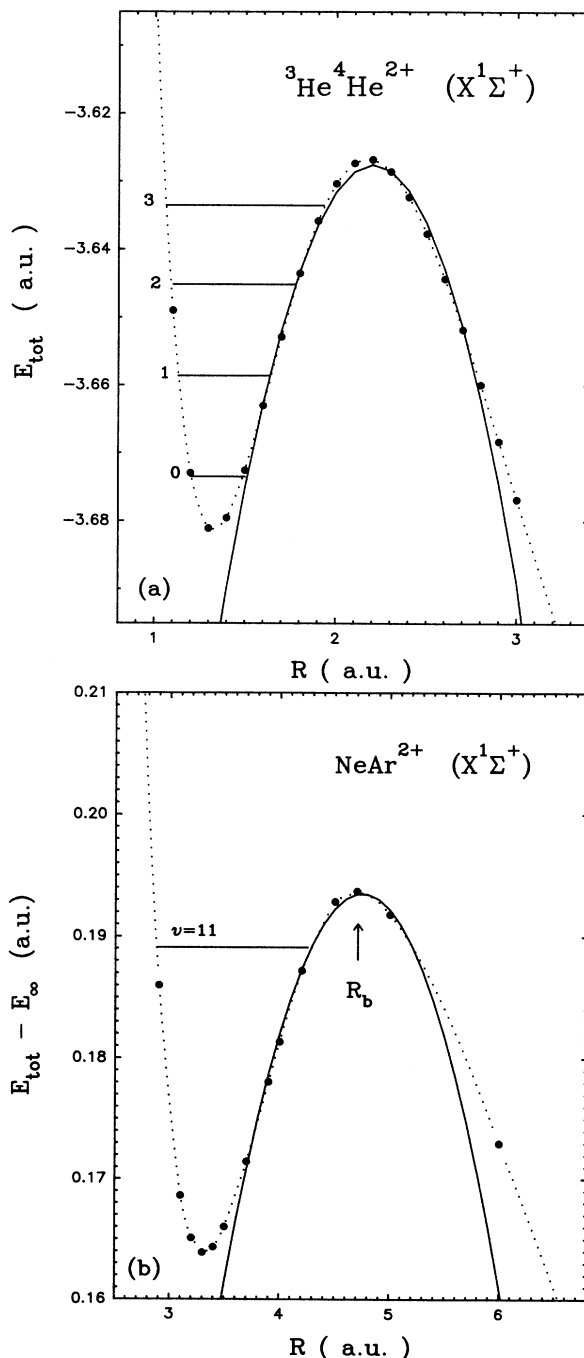


FIG. 1. The metastable potential-energy curves for the ground states of (a) ${}^3\text{He}^4\text{He}^{2+}$ from Ref. [3] and (b) ${}^{20}\text{Ne}^{40}\text{Ar}^{2+}$ from Ref. [11], The parabolic model potential barrier fitted for $l=0$: - - - - -.

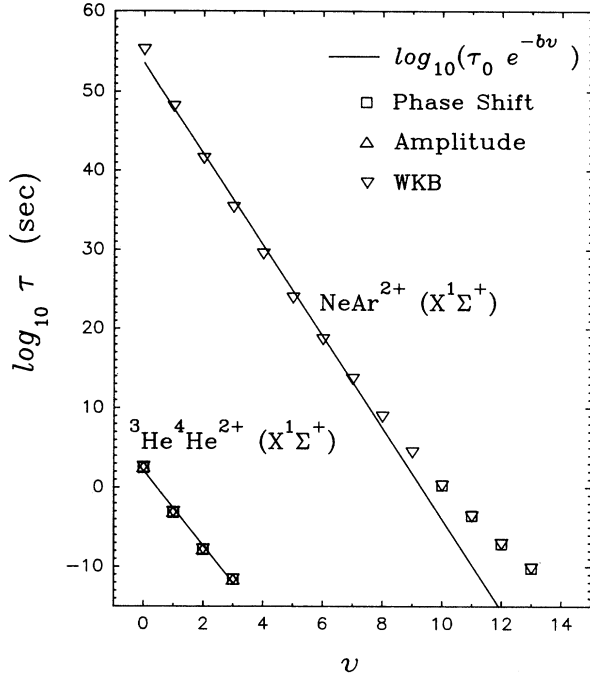


FIG. 2. The dependence of the mean lifetimes of the $l = 0$ states of ${}^3\text{He}^4\text{He}^{2+}$ and ${}^{20}\text{Ne}^{40}\text{Ar}^{2+}$ on the vibrational quantum number ν . (Amplitude method from Ref. [6]; WKB calculations for ${}^3\text{He}^4\text{He}^{2+}$ from Ref. [2].)

where $x_l = x - \frac{c}{2}$ is the distance from the shifted barrier maximum, and $c = \frac{l(l+1)}{2\mu\alpha_0 R_b^3} \left[\frac{1}{1 - \frac{3l(l+1)}{2\mu\alpha_0 R_b^4}} \right]$. The relationship between the fit parameters of a state with angular momentum l and the $l = 0$ state are then given to first order in $l(l+1)$ by

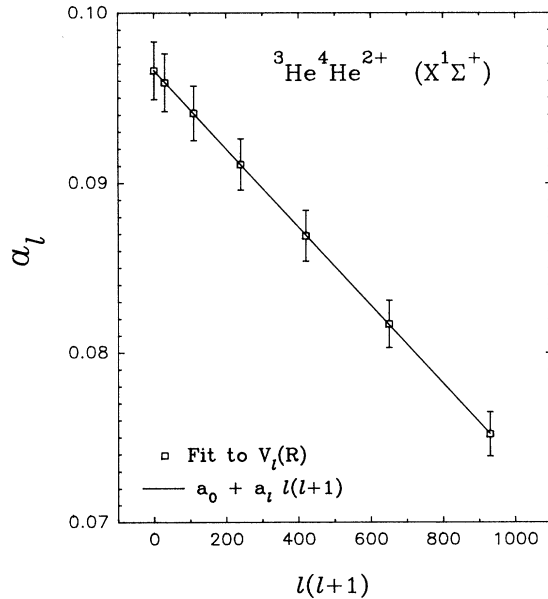


FIG. 3. The dependence of a_l on $l(l+1)$, symbols from the fit of $U_l - a_l (R - R_b)^2$ to the ${}^3\text{He}^4\text{He}^{2+}$ potential-energy curve for different rotational states, i.e., $V_l(R) = V_0(R) + l(l+1)/2\mu R^2$ where $V_0(R)$ is the potential curve given in Fig. 1.

$$U_l \simeq U_0 + \frac{l(l+1)}{2\mu R_b^2},$$

and

$$a_l \simeq a_0 - \frac{3l(l+1)}{2\mu R_b^4}. \quad (10)$$

By fitting $U_l - a_l x_l^2$ to the actual potential curve $V_0(R) + \frac{l(l+1)}{2\mu R^2}$ for angular momentum l , around the top of the barrier, we found that a_l indeed depends linearly on $l(l+1)$ (see Fig. 3). For the ${}^3\text{He}^4\text{He}^{2+}$ system, the

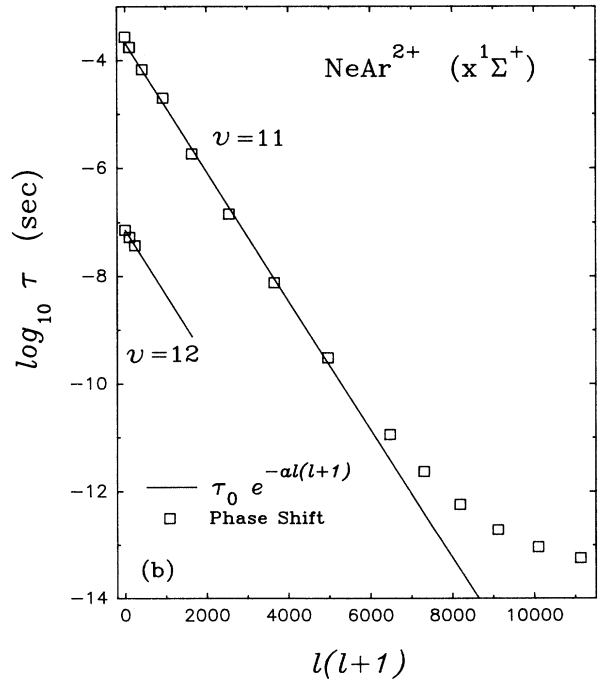
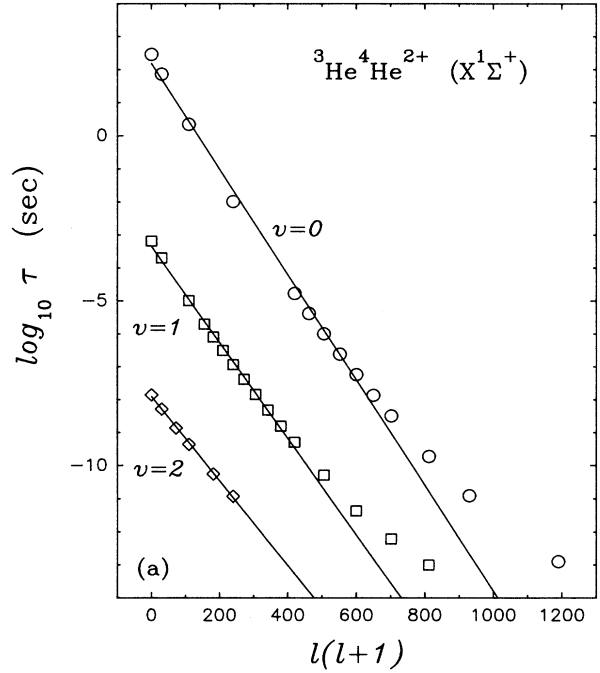


FIG. 4. The dependence of the mean lifetimes of some vibrational states of (a) ${}^3\text{He}^4\text{He}^{2+}$ and (b) ${}^{20}\text{Ne}^{40}\text{Ar}^{2+}$ on $l(l+1)$.

slope predicted using Eq. (10), 2×10^{-5} , is in accord with the slope derived from the fit, 2.3×10^{-5} .

The energy levels for the rovibrational states v, l are given approximately by $E_{vl} = E_{v0} + l(l+1)/2\mu R_0^2$, where E_{v0} is the energy of the vibrational level v for $l = 0$ and the second term is the energy of a rigid rotor with angular momentum l . Using a similar first order expansion in $l(l+1)$ one can easily show that the turning points of the parabolic potential barrier, $\pm b_l$, which are solutions

$$\tau_{vl} = f_{vl}^{-1} e^{\pi\sqrt{2\mu a_0} b_0^2 \left[1 + \frac{3l(l+1)}{2\mu R_0^2 a_0} + \frac{l(l+1)}{2\mu b_0^2 R_0^2 a_0} - \frac{l(l+1)}{2\mu b_0^2 R_0^2 a_0} \right]} \sqrt{1 - \frac{3l(l+1)}{4\mu R_0^2 a_0}}. \quad (12)$$

Expanding the last square root in the exponential and keeping only terms to first order in $l(l+1)$ yields

$$\tau_{vl} = f_{vl}^{-1} e^{\pi\sqrt{2\mu/a_0} (U_0 - E_{v0}) \left[1 + \frac{l(l+1)}{2\mu R_0^2 (U_0 - E_{v0})} - \frac{l(l+1)}{2\mu R_0^2 (U_0 - E_{v0})} + \frac{3l(l+1)}{4\mu R_0^2 a_0} \right]}, \quad (13)$$

which can be rewritten as (neglecting the dependence of f_{vl} on v and l)

$$\tau_{vl} \propto e^{-\alpha l(l+1)}, \quad (14)$$

where

$$\alpha \simeq \frac{\pi}{\sqrt{2\mu a_0}} \left(\frac{1}{R_0^2} - \frac{1}{R_b^2} - \frac{3(U_0 - E_{v0})}{2a_0 R_0^4} \right). \quad (15)$$

The relation in Eq. (14) is the scaling law for the mean lifetime of a given vibrational state v with the angular-momentum quantum number l . Notice that this model suggests similar exponential dependence of τ on $l(l+1)$ for different vibrational states of the same metastable potential-energy curve because typically $\frac{3(U_0 - E_{v0})}{2a_0 R_0^4} \ll \left(\frac{1}{R_0^2} - \frac{1}{R_b^2} \right)$ [see Eq. (15)].

The mean lifetimes of $v = 0, 1$, and 2 vibrational states of the metastable ${}^3\text{He}^4\text{He}^{2+}$ molecular ion as a function of $l(l+1)$, are shown in Fig. 4(a). It is clear that the mean lifetimes follow approximately the scaling law of Eq. (14). Furthermore, the slopes are nearly the same. Specifically, the values of α evaluated from the fit to the mean lifetimes calculated using the phase-shift method are $\alpha_{fit} = (3.77 \pm 0.07) \times 10^{-2}$, $(3.54 \pm 0.05) \times 10^{-2}$, and $(3.24 \pm 0.05) \times 10^{-2}$ for $v = 0, 1$, and 2, respectively. These are to be compared to the values obtained from Eq. (15), $\alpha_{model} = 4.02 \times 10^{-2}$, 4.14×10^{-2} , and 4.26×10^{-2} , respectively. The slow decrease of α with increasing v from the fitting is, however, in contradiction with the slow increase predicted by Eq. (15). This may be due to the neglect of the dependence of v and l in f_{vl} within our model.

Similar comparison is made in Fig. 4(b) for the dependence of the mean lifetimes of the rotational excited

of the condition $U_l - a_l b_l^2 = E_{vl}$, are given by

$$b_l^2 \simeq b_0^2 \left(1 + \frac{3l(l+1)}{2\mu R_b^4 a_0} + \frac{l(l+1)}{2\mu b_0^2 R_0^2 a_0} - \frac{l(l+1)}{2\mu b_0^2 R_0^2 a_0} \right), \quad (11)$$

where $b_0 = \pm\sqrt{(U_0 - E_{v0})/a_0}$ are the turning points for $l = 0$. Substituting the values of a_l and b_l from Eq. (10) and Eq. (11), respectively, into Eq. (6) yields the following expression for the mean lifetime of the v, l state:

states for $v = 11$ of the ${}^{20}\text{Ne}^{40}\text{Ar}^{2+}$ molecular ion. The dependence on $l(l+1)$ again is well represented by Eq. (14) and the value of α obtained from the fit, $(2.75 \pm 0.03) \times 10^{-3}$, compares well with 4.39×10^{-3} from Eq. (15). The difference is much larger than for ${}^3\text{He}^4\text{He}^{2+}$, but such discrepancy can be understood since we have shown already that the present simple model does not apply to higher vibrational states where the anharmonicity becomes large. In fact, the scaling law breaks down also for high- l states, as can be seen in Fig. 4(b). For the high- l and/or high- v states, the assumptions used in the derivation of the scaling laws given in Eq. (2) and Eq. (3) do not apply.

To conclude, we have shown that the mean lifetimes of metastable molecular states which dissociate by tunneling through the potential-energy barrier exhibit an exponential decrease with increasing vibrational quantum number v , and with increasing $l(l+1)$ for states with angular momentum l . Based on the WKB model and a number of approximations on the potential near the barrier, we have shown how these relations can be derived analytically. These simple scaling laws are shown to break down for large values of v and l , where the energies of these states cannot be obtained using the simple harmonic oscillator and rigid rotator approximations.

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