

Theory of the optical spectrum of Na₂ on ⁴He droplets: effects of the zero-point energy of the nearest atoms

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Abstract. An analytical theory of the optical transitions of a molecule bound at the surface of a ⁴He droplet is developed for the case of a strong softening of the excited-state nearest neighbor dynamics. The optical bandwidth is found to be determined by the zero-point kinetic energy released at the transition. The theory is applied to the triplet-triplet optical transition in Na₂ molecule, for which an asymmetric vibronic band with no pronounced zero-phonon line is predicted, in good agreement with the experiment.

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1 Introduction

Small alkali molecules bound at the surface of quantum clusters appear to be a unique system with possibly one of the weakest interatomic interactions in nature [1,2]. An opportunity to study these interactions is offered by optical spectroscopy, as demonstrated by Stienkemeier et al. laser-induced fluorescence studies of the vibronic structure in the triplet-state optical spectra of sodium dimers and trimers on small ⁴He droplets [3–5]. The $1^3\Sigma_g^+ \leftarrow 1^3\Sigma_u^+$ excitation spectrum in the region between 14500 and 14900 cm⁻¹ consists of several narrow bands corresponding to different high vibrational levels of the molecule in the excited $1^3\Sigma_g^+$ state. The small and yet remarkable half-width of 30 cm⁻¹ is a consequence of the interaction of the molecule with the droplet [3–5].

Taking into account that the interaction of the optical electron of the molecule in the triplet state with the vibrations of the droplet (phonons) is rather weak, one would expect to observe the zero-phonon lines (ZPLs) and the relatively weak phonon wings separated from ZPLs by dips. On the contrary the bands observed in the region between 14500 and 14900 cm⁻¹ have no pronounced ZPLs and no dips on the blue side. Instead, they are characterized by a triangular shape with a steep rise on the red side and a slow decay on the blue side. Note that in the spectral region between 15800 and 16500 cm⁻¹, corresponding to the electronic transitions between singlet states, sharp ZPLs are indeed observed with a width of only about 0.8 cm⁻¹ and relatively broad (~80 cm⁻¹) phonon-assisted bands [4,5].

A remarkable peculiarity of the optical transitions involving Na₂ triplet states, which makes them so different from the ones between singlet states, is the large equilibrium distance (~5 Å) between Na atoms in the ground *ungerade* triplet state due to the Pauli principle. In the excited *gerade* triplet state the molecular bond length is much shorter (~3.5 Å) [6]. As a result the excitation takes place mostly to highly excited vibrational levels ($n \geq 24$) [7]. Thus the mean amplitude of the vibrations in these levels is large (2.5 to 3 Å for levels 24 to 30) and comparable to the distance between ⁴He atoms in the droplet. Moreover, the mean velocity of Na atoms in these vibrational levels is comparable with the mean velocity of the zero-point vibrations of ⁴He atoms in the droplet. Due to such coincidence of parameters, one may expect a strong coupling of a molecule to the dynamics of the few nearest ⁴He atoms.

In general the He atom density has large (Friedel) oscillations around an impurity molecule, with a maximum at a few Å from the molecule center (“snowball” effect) [8]. Such density oscillations occur also around a surface impurity atom [9], and are expected to induce a localized phonon excitation near the bulk maxon frequency, just as found for molecules inside the droplet [10]. Thus it may be assumed that the sudden contraction of the Na₂ molecule diameter by as much as 1.5 Å yields a strong softening of the localized snowball phonon. This means a strong increase of the interaction of the optical electrons with snowball low-energy phonons [11]. As a result the ZPL disappears in the spectrum and the low-energy part of the phonon sideband is strongly enhanced. Taking into account that the zero-point energy of the initial bound state of few atoms is almost fully released at the transition, one

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can conclude that the width of the band is determined by the zero-point energy of these atoms. More precisely, the kinetic energy of the zero-point motion of the atoms gives here the main contribution. This follows from the Franck-Condon principle according to which the coordinates and momenta of atoms are conserved at the transition. However, in the case under consideration the energy of the final state depends but weakly on the coordinates.

2 Theory

In order to calculate the optical bands for the case described above one must take into account that the potential energy of the final (excited) electronic state of a molecule very weakly depends on some coordinates of the droplet, whereby this dependence is remarkable in the initial state. In this case, there is a large relative change (softening) of the local phonon dynamics associated with the transition, which has to be taken into account.

In dealing with the absorption and emission spectra of optical centers in the condensed matter the so-called basic model is conveniently used, where only the linear electron-phonon interaction is considered (see, e.g., Refs. [12–14]). However, if the change of the local phonon dynamics is important, also the quadratic electron-phonon interaction needs to be included. This strongly complicates the solution of the problem since the electronic transition yields a mixing of all the vibrational modes contributing to the process. For free molecules with a small number of contributing vibrational modes the problem can be solved by applying the density matrix method [15], as has been done, e.g., in reference [16]. In the present case, however, this approach is inapplicable since the number of contributing modes of the droplet (phonons) is very large. The problem is similar to that of electron-phonon transitions at impurity centers in crystals, where the entire density of bulk phonon states projected onto the local coordinates is involved, the only selection being that of point symmetry. Due to the surface location of the Na dimer the local symmetry is very low, so that, in principle, the whole spectrum of droplet excitations may be involved.

In the case of a relatively small change of the local force constants induced by the electronic transition, the problem can be solved by applying the time-ordering expansion method (see, e.g., [17,18]). If the force constant changes are not small, then the numerical method [19] based on path integrals can be applied (some results of calculations by this method are given in [20,21]). However, as we have recently shown [11], in the case of a large relative change (softening) of the local phonon dynamics an analytical derivation is also possible thanks to the small ratio of the mean local vibrational frequencies in the final electronic state to the initial ones. In reference [11] a purely quadratic vibronic coupling was considered. Here both quadratic and linear coupling terms shall be taken into account.

We restrict ourselves to the harmonic and Condon approximations. Then the Fourier transform of the spectrum

is given by the Lax [22] equation (with $\hbar = 1$)

$$F(t) = \langle e^{itH_2} e^{-itH_1} \rangle, \quad (1)$$

where $\langle \dots \rangle$ is the quantum-statistical averaging,

$$H_1 = \sum_j \omega_{1j} (a_{1j}^+ a_{1j} + \frac{1}{2}) \quad (2)$$

$$H_2 = H_1 + V \quad (3)$$

are the vibrational Hamiltonians in the initial (index 1) and final (index 2) electronic states, respectively; ω_{1j} are the phonon frequencies, a_{1j} and a_{1j}^+ are the respective annihilation and creation operators in the initial state.

$$V = V_0 + a_0 q + \frac{1}{2} q b q \quad (4)$$

is the sum of the static (V_0) and dynamic changes in the vibrational potential due to the electronic transition. The latter contains a linear and a quadratic term, weighed by the respective electron-phonon coupling constants a_0 and b , in the configurational coordinate operator

$$q = \sum_j e_{1j} (a_{1j} + a_{1j}^+) / \sqrt{2\omega_{1j}}, \quad (5)$$

with e_{1j} , the j th phonon polarization vector in the initial electronic state describing the motion of the He atoms surrounding the Na₂ molecule.

Our approach is based on the Fourier-amplitude method [21] which uses both Hamiltonians, H_1 and H_2 , in the diagonal representation. In such a representation H_2 reads

$$H_2 = \sum_k \omega_{2k} (a_{2k}^+ a_{2k} + \frac{1}{2}) \quad (6)$$

where ω_{2k} are the phonon frequencies, and a_{2k} , a_{2k}^+ the respective annihilation and creation operators in the final electronic states. The phonon operators a_{2k} , a_{1j} and a_{2k}^+ , a_{1j}^+ are related by the Bogolyubov transformation [11,23]

$$a_{2k}^+ = \xi_{2k} + \sum_j \frac{c_{jk}}{2\sqrt{\omega_{1j}\omega_{2k}}} [(\omega_{1j} + \omega_{2k})a_{1j}^+ + (\omega_{2k} - \omega_{1j})a_{1j}], \quad (7)$$

$$a_{1j}^+ = -\xi_{1j} + \sum_k \frac{c_{jk}}{2\sqrt{\omega_{1j}\omega_{2k}}} [(\omega_{1j} + \omega_{2k})a_{2k}^+ + (\omega_{1j} - \omega_{2k})a_{2k}], \quad (8)$$

where $\xi_{2k} = a_0 e_{2k} / \sqrt{2\omega_{2k}^3}$ and $\xi_{1j} = \bar{a}_0 e_{1j} / \sqrt{2\omega_{1j}^3}$ are the constant contributions, $\bar{a}_0 = a_0 - bq_0$, $q_0 = a_0 \sum_k e_{2k}^2 / \omega_{2k}^2$ is the value of q in the minimum of the potential energy in the final state, e_{2k} and e_{1j} are the final-state k th phonon and the initial-state j th phonon polarization vectors, respectively. They are linearly related by $e_{2k} = \sum_j c_{jk} e_{1j}$ where,

$$c_{jk} = b \frac{e_{1j} e_{2k}}{\omega_{2k}^2 - \omega_{1j}^2} \quad (9)$$

is the orthogonal Duschinsky rotation matrix describing the phonon mixing due to the quadratic term. The excited (ground) state eigenvalues ω_{2k} (ω_{1j}) are viewed as

originating from the perturbation b ($-b$) of the ground (excited)-state eigenfrequencies ω_{1j} (ω_{2k}). They are the zeroes of the equations

$$\operatorname{Re}[1 - bg_1(\omega^2 + i0^+)] = 0, \quad \operatorname{Re}[1 + bg_2(\omega^2 + i0^+)] = 0, \quad (10)$$

where

$$g_{1(2)}(z) = \sum_{j(k)} \frac{e_{1j}^2(2k)}{z - \omega_{1j}^2(2k)} \quad (11)$$

is the projected ground-state (excited-state) Green's function. Thus,

$$\sum_j \frac{be_{1j}^2}{\omega_{2k}^2 - \omega_{1j}^2} = \sum_k \frac{be_{2k}^2}{\omega_{2k}^2 - \omega_{1j}^2} = 1. \quad (12)$$

We specially refer to the zero-temperature case and calculate the time derivative

$$-i \frac{dF}{dt} = \delta_0 F + \frac{a_0}{\sqrt{2}} A + \frac{b}{4} P, \quad (13)$$

where

$$\begin{aligned} \delta_0 &= b \sum_j e_{1j}^2 / 4\omega_{1j}, & A &= \sum_j \frac{e_{1j} A_j}{\sqrt{\omega_{1j}}} \\ P &= \sum_j \frac{e_{1j} e_{1j'} p_{jj'}}{\sqrt{\omega_{1j} \omega_{1j'}}} \end{aligned} \quad (14)$$

and

$$A_j = \langle 0 | \hat{F} a_{1j}^+ | 0 \rangle, \quad p_{jj'} = \langle 0 | \hat{F} a_{1j}^+ a_{1j'}^+ | 0 \rangle \quad (15)$$

are the one- and two-phonon Fourier amplitudes, respectively, with $\hat{F} \equiv \exp[it(H_2 - E_0)]$, and E_0 is the energy of the zero-point phonon state $|0\rangle$ in the initial electronic state.

The creation operator a_{1j}^+ in the Fourier amplitudes can be expressed via a_{2k} and a_{2k}^+ by means of equation (8). Then one can shift the latter operator to the left according to the rule $e^{itH_2} a_{2k}^+ = e^{it\omega_{2k}} a_{2k}^+ e^{itH_2}$, express the operators a_{2k} and a_{2k}^+ via a_{1j} and a_{1j}^+ and take into account that $a_{1j} |0\rangle = \langle 0 | a_{1j}^+ = 0$. As a result, one gets the linear equation for the Fourier amplitudes [23] (see also [11]).

In general, due to the large number of phonons, the equations for the Fourier amplitudes cannot be solved. However, in the case under consideration, where the mean vibrational frequency in the excited state is small as compared to the mean frequency in the initial state, one can use the approximation

$$c_{jk} \approx -b e_{1j} e_{2k} / \omega_{1j}^2, \quad (16)$$

which allows for a factorization of equations and their straightforward solution. By introducing the negative moments of the local phonon density of states

$$f_n \equiv \sum_j e_{1j}^2 \omega_{1j}^{-n}, \quad (17)$$

it can be shown that in the present case $b \approx -1/f_2$.

Since the observed optical bands do not display any specific phonon structure [3], the analysis may be restricted to the envelopes of optical bands. The latter is described by the asymptotic form of the Fourier transform $F(t)$ at small times (the calculations of $F(t)$ for an arbitrary t will be given elsewhere), which allows one to write $\exp[it\omega_{2k}] \cong 1 + it\omega_{2k}$. The equations for the Fourier amplitudes are then found to be

$$A_j = it\beta_j F(t) + \sum_{j'} s_{jj'} \sqrt{\omega_{1j'}} A_{j'} \quad (18)$$

$$p_{jj'} = g_{jj'} F - it\beta_j A_{j'} + \sum_{j_1} g_{jj_1} (p_{j_1 j'} + r_{j_1 j'}) - \frac{it\omega_{1j'}}{2} r_{jj'}, \quad (19)$$

where

$$\begin{aligned} r_{jj'} &= \langle 0 | a_{1j} \hat{F} a_{1j'}^+ | 0 \rangle = p_{jj'} + \frac{it\omega_{1j'}}{2} (r_{jj'} - p_{jj'}) \\ &\quad + \frac{it\omega_{1j}}{2} F \delta_{jj'} \end{aligned} \quad (20)$$

and

$$\begin{aligned} \beta_j &= a_0 \sqrt{\frac{\omega_{1j}}{8}} \sum_k \frac{c_{jk} e_{2k}}{\omega_{2k}}, & s_{jj'} &= - \sum_k \frac{c_{jk} e_{j'k}}{\omega_{2k}}, \\ g_{jj'} &= \sqrt{\omega_{1j} \omega_{1j'}} \frac{s_{jj'}}{2}. \end{aligned} \quad (21)$$

In these equations, the terms $\propto \omega_{2k}$ have been omitted, because they give a much smaller contribution than the terms $\propto \omega_{1j} \omega_{1j'} / \omega_{2k}$ and $\propto \omega_{1j} \pm \omega_{1j'}$.

Let us consider the one-phonon Fourier amplitude. By using equations (18) and (16) it is found that

$$A \approx \phi \left[it \left(a_0 / \sqrt{2} \right) F + f_2^{-1} \bar{A} \right], \quad (22)$$

where $\phi = \sum_k e_{2k}^2 \omega_{2k}^{-1}$, and $\bar{A} = \sum_j \omega_{1j}^{-1} A_j$. The latter amplitude satisfies the same equation (18), but with the additional factor f_3/f_2 . Taking into account that $\phi \approx f_2^2/f_3$, one obtains $A \approx it \left(a_0 f_2^2 / \sqrt{2} f_3 \right) F$.

Analogously one can find the equations for the two-phonon Fourier amplitudes:

$$P \approx \frac{1}{2} \phi F + \frac{it\phi a_0}{\sqrt{2}} A - \frac{\phi}{2f_2} \bar{P} - \frac{1}{2f_2} (\phi + it) \bar{R}, \quad (23)$$

$$\bar{R} \approx \bar{P} + \frac{itf_3}{2f_2} F + \frac{itf_3}{2f_2^2} (\bar{R} - \bar{P}), \quad (24)$$

where $\bar{P} \approx P f_3 / f_2$. Solving these equations, we find for a small t

$$P \approx \frac{f_2^2}{f_3} \left(1 + \frac{1}{2} a_0^2 t^2 + \frac{1}{1 - itf_3 / 2f_2^2} \right) F. \quad (25)$$

As a result, we get the following equation:

$$-i \frac{d \ln F}{dt} \approx \delta + \frac{1}{2} \omega_1^2 a^2 \left(it + \frac{\omega_1 t^2}{4} \right) + \frac{\mu \omega_1 / 2}{1 - it\omega_1 / 2}, \quad (26)$$

where

$$\mu = \frac{f_2^3}{2f_3^2}, \quad a = a_0 \frac{f_2^3}{f_3^{3/2}}, \quad \omega_1 = \frac{f_3}{f_2}, \quad \delta = -\frac{f_1}{4f_2} - \frac{f_2}{4f_3}. \quad (27)$$

Equation (26) can easily be integrated to give:

$$F(t) = (1 - i\omega_1 t/2)^{-\mu} \exp [i\delta t - a^2 \omega_1^2 t^2 (6 - i\omega_1 t)/24]. \quad (28)$$

Equation (28) was first derived in the $a = 0$ limit in reference [11]. For $\mu = 0.5$ equation (28) coincides with the corresponding equation in a single-mode case (see Appendix).

As it follows from equation (28), the phonon continuum in the case of a sufficiently small linear interaction parameter a manifests itself in the shape of the spectral band principally through the parameter μ . The latter is chiefly determined by the low-frequency part of the phonon spectrum, which essentially depends on the dimensionality D of the phonon system. If the Debye model is applied (with a unity Debye frequency), then

$$e_1^2(\omega) = \sum_j e_{1j}^2 \delta(\omega - \omega_{1j}) = (D + 2) \omega^{D+1}. \quad (29)$$

In the $D = 3$ case $\mu = 0.37$, while for $D = 2$ it is $\mu = 0.25$. In the Debye-van Hove model, where $e_1^2(\omega) \propto \omega^{D+1} \sqrt{1 - \omega^2}$, $\mu = 0.35$ for $D = 3$ and $\mu = 0.23$ for $D = 2$. In all cases the values of μ remarkably differ from $\mu = 0.5$ valid for a single-mode case. The frequency parameter ω_1 , which determines the width of the band, is not very sensitive to the details of the phonon spectrum. For example, in the $D = 3$ case it equals 0.9 for the Debye model and 0.85 for the Debye-van Hove model. For $D = 2$ it equals 0.9 for the Debye-van Hove model and 1 for the Debye model. In a single-mode case it also equals 1. The terms $\propto a^2$ in equation (28) take into account the effect of the acceleration in the final state, whereas the term $\propto ia^2 t^3$ describes the Airy oscillations.

3 Results and discussion

The present theory is now applied to the optical spectra of Na_2 in the triplet state on the surface of a He_4 droplet. To that end, we must include to the process the contributions of several configurational coordinates q . Since ω_1 is weakly dependent on the details of the phonon spectrum, one single value of ω_1 is used for all coordinates. In this way also in the case of several coordinates q the Fourier transform of the spectral band is determined by equation (28) with μ and a^2 replaced by the respective sums over μ and a^2 for each coordinate. It is also assumed that bulk (3D) and surface (2D) phonons make comparable contributions to these coordinates so that a mean value $\mu = 0.3$ may be attributed to each configurational coordinate, and for a number of 4 to 7 nearest-neighbor He atoms a total μ varying between 1.2 and 2.1 is considered in the calculations.

The theoretical spectra, calculated as the functions of ω/ω_1 for a set of μ values in the above range and for

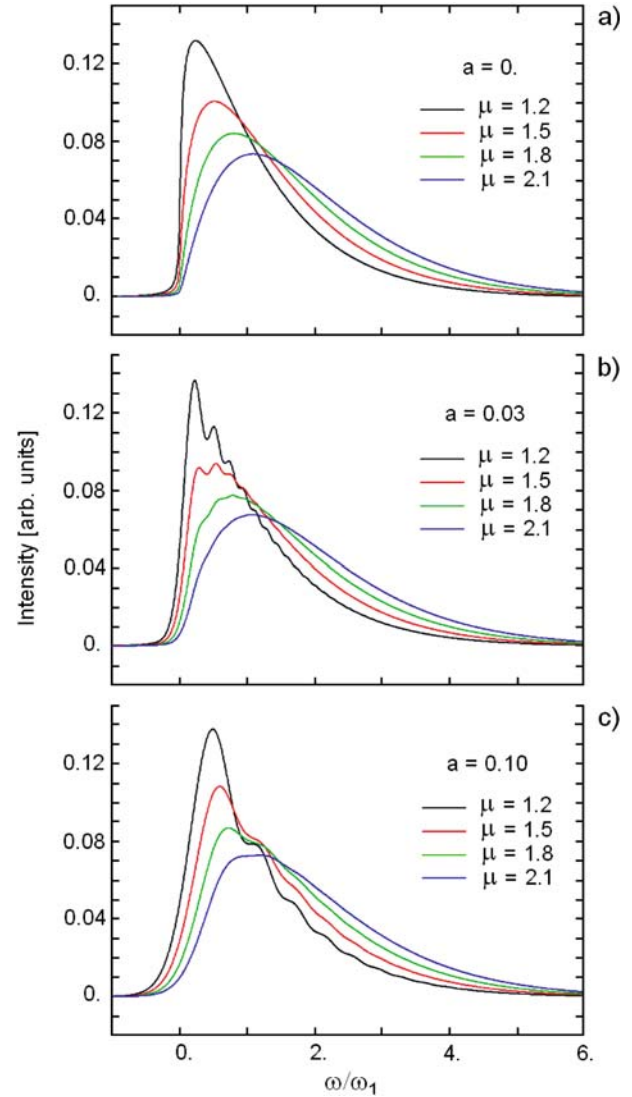


Fig. 1. Computed spectral shapes for the $1^3\Sigma_g^+ \leftarrow 1^3\Sigma_u^+$ transition in Na_2 on the surface of a ^4He droplet for different values of the parameters μ and a (see text) and for $\omega_1 = 0.9 \omega_m = 10.4 \text{ cm}^{-1}$.

three representative values of $a = 0, 0.03$ and 0.1 , are displayed in Figures 1a–1c. The frequency parameter ω_1 has been chosen to be $0.9\omega_m$, where $\omega_m = 10.4 \text{ cm}^{-1}$ is the maximum phonon (*maxon*) frequency for ^4He droplets as derived from fitting the roton/*maxon* sidebands of the absorption spectrum of glyoxal-doped droplets [24]. The fine structure near the peak in the theoretical spectra for $a \neq 0$ and the smaller values of μ reflects the Airy oscillations [25]. Since they would have a different period for different values of ω_1 , these oscillations should be, most probably, washed out in a more realistic calculation where even slightly different values of ω_1 would be attributed to different configurational coordinates. Despite the simplifying assumptions made in the present calculations, the resulting width and the shape of the spectra for small a show a general agreement with the experimental spectra reported in references [3–5]. As shown in Figure 2a the

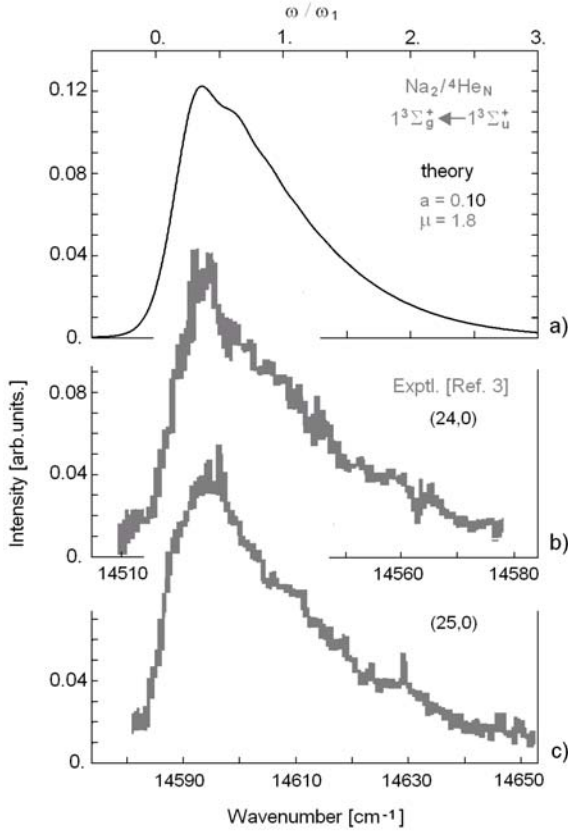


Fig. 2. Comparison between the theoretical spectrum for $a = 0.10$ and $\mu = 1.8$ (a) and the experimental (24, 0) and (23, 0) vibronic spectra (b, c) associated with the $1^3\Sigma_g^+ \leftarrow 1^3\Sigma_u^+$ transition in the Na₂ dimer trapped at the surface of a ⁴He droplet as measured by Stienkemeier et al. [3–5].

theoretical spectrum for $a = 0.10$ and $\mu = 1.8$ reproduces quite well a typical triangular shape of both the experimental (24, 0) and (23, 0) vibronic spectra associated with the $1^3\Sigma_g^+ \leftarrow 1^3\Sigma_u^+$ transition of Na₂ on a ⁴He droplet as measured by Stienkemeier et al. [3–5] (Figs. 2b, 2c).

It should be noted that the vibrational amplitudes of the molecule Na₂ for low- and high-vibrational levels are rather different, such difference being related to the distance between He atoms. Therefore, the number of contributing configurational coordinates remarkably increases with the vibrational level of the molecule. This allows one to expect an increase of μ with the vibrational number n of the molecule in the excited triplet state. This should cause the increase of the bandwidth and the decrease of its asymmetry with an increasing number n of the vibrational level. It would be of interest to experimentally check this prediction of the theory. With the decreasing size of the He droplet one should also expect a decrease of μ and therefore of the bandwidth. The presently available data unfortunately do not allow one to check these predictions. Hopefully the present study will stimulate further experimental investigations.

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Appendix

Let us consider a single-coordinate case with quadratic and linear potential energies in the initial and final states. In this case

$$H_1 = p^2/2 + x^2/2, \quad H_2 = p^2/2 + ax, \quad (\text{A.1})$$

where x is the dimensionless coordinate operator, p is the dimensionless momentum operator (in corresponding units $\omega_1 = 1$). The Fourier transform of the spectrum in the zero-temperature case can be presented in the form

$$F(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dE |\langle E | 0 \rangle|^2 e^{it(E-E_0)}, \quad (\text{A.2})$$

with $E_0 = 1/2$, $|E\rangle$ is the eigenstate of the Hamiltonian H_2 with the energy E . We are using the momentum representation. In this representation the zero-point state of the oscillator with the unit frequency reads

$$|0\rangle = (\pi)^{-1/4} \exp(-p^2/2), \quad (\text{A.3})$$

and the stationary Schrödinger equation of the Hamiltonian H_2 gets the form

$$(p^2/2 + iad/dp) |E\rangle = E |E\rangle. \quad (\text{A.4})$$

(Remember that in the momentum representation $x = id/dp$.) The solution of this equation is as follows:

$$|E\rangle = a^{-1/2} \exp [i(p^3/6a - Ep/a)]. \quad (\text{A.5})$$

Inserting equations (A3) and (A5) into (A2), one gets

$$F(t) = \frac{1}{2a\sqrt{\pi^3}} \int_{-\infty}^{\infty} dE e^{i(E-E_0)t} \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dp' e^{-p^2/2} \times e^{i(p^3/6a - Ep/a)} e^{-i(p'^3/6a - Ep'/a)} e^{-p'^2/2}. \quad (\text{A.6})$$

The integral over E gives $2\pi \delta(t - p/a + p'/a)$. After integration over p' we find

$$F(t) = \frac{1}{\sqrt{\pi}} e^{-it/2 - a^2 t^2 (1-it/3)/2} \int_{-\infty}^{\infty} dp e^{(atp - p^2)(1-it/2)}. \quad (\text{A.7})$$

The last (Poisson) integral over p gives

$$F(t) = \frac{1}{\sqrt{1-it/2}} e^{-it/2 - a^2 t^2 (6-it)/24}. \quad (\text{A.8})$$

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