Fractional Quantization of Molecular Pseudorotation in Na_3

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(Received 17 March 1986)

Fractional quantization of the adiabatic pseudorotation in an isolated molecule is reported. This result, concerning the large-amplitude pseudorotation in $2^2E'$ Na_3, constitutes the first direct verification of the adiabatic sign-change theorem, and also presents the most complete picture of the level structure and internuclear dynamics of a metal-atom cluster yet given.

PACS numbers: 36.40.+d

The adiabatic theorem of quantum mechanics states that a system in an eigenstate $\Psi_n(R(t))$ responds to slowly varying changes in its parameters $R(t)$ such that the system remains in the same eigenstate, apart from an acquired phase.[1] In an unexpected recent development, Berry[2] discovered a major omission in this theorem, namely that if the parameters complete a circuit in c in a parameter space, then the acquired phase is not simply the familiar dynamical phase $(i\hbar)^{-1}\int E(R(t))\,dt$. Instead an additional, geometrical phase $\gamma_n(c)$ may result. The origins of this additional phase are anholonomic, that is, they depend only on the geometry of the parameter space and the circuit traversed.

The geometrical phase $\gamma_n(c)$ arises from rather general considerations and thus is relevant to many areas of quantum physics.[2,3] Condensed matter applications have been found in the statistics pertaining to the fractional quantization of the Hall conductance and to linear-chain conductors.[4-6] Wilczek and Zee have presented a generalization of this new theorem to degenerate subspaces, to show how non-Abelian gauge fields and altered quantization conditions arise in simple adiabatic systems.[7]

A further motivating consideration is the behavior of Born-Oppenheimer wave functions in molecules. A significant result first noticed in 1963 by Herzberg and Longuet-Higgins[8] relates to adiabatic excursions of such wave functions in the neighborhood of an electronic degeneracy. They show that, if the internuclear coordinates traverse a circuit within which the state is degenerate with another, then the electronic wave function Ψ_e acquires an additional phase of π, i.e., it changes sign. This sign change, which can now be recognized as a special case $[\gamma_n(c)=\pi]$ of Berry's geometrical phase, applies to the adiabatic electronic states of a large class of molecular systems exhibiting conical intersections. Its corollary is that the stationary vibrational wave function $\chi(R)$ must also change sign when taken through this closed path, to make the total product wave function, $\Psi_e(R)\chi(R)$, single valued. This result explains the long-standing prediction, concerning model systems representing the dynamical Jahn-Teller effect, that the quantum number for the pseudorotation takes on fractional values even in the absence of spin.[9]

Notably lacking are observations on real molecular systems demonstrating the existence of this effect. Especially attractive from the theoretical viewpoint is the high permutational symmetry of X_n systems (atomic clusters). The alkali clusters in particular are often cited as models.[10,11] In 1979 Herrmann *et al.*[12] reported the first absorption spectrum of gas-phase Na_3. These data are too congested to assign, but the recent use of an ultracold cluster beam source has greatly simplified the spectrum,[13,14] revealing detailed vibrational fine structure and rotational band profiles. Figure 1(a) shows the structured part of the absorption spectrum of supersonically cooled Na_3 ($T_{rot} < 10$ K, $T_{vib} < 100$ K) recorded by means of resonant two-photon ionization spectroscopy. The present work focuses on the region from 600 to 625 nm [Fig. 1(b)], presenting a complete assignment of its complex band system. As a direct consequence of this assignment we find compelling evidence for half-odd quantization

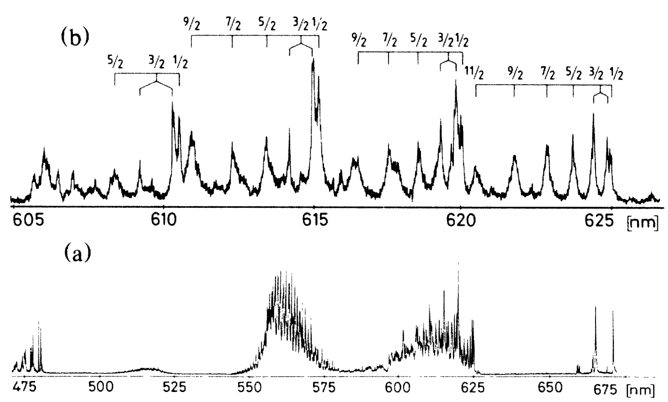

FIG. 1. (a) Resonant two-photon ionization spectrum of Na_3 in the visible region. Spectra in different regions are not rigorously normalized to variation in dye laser parameters. (b) Expanded spectrum of the region 600–625 nm. State labels correspond to assignment given in the text.

of the free molecular pseudorotation, thus offering the first experimental confirmation of the sign-change theorem and direct measurement of $\gamma_n(c)$.

Sodium clusters are produced by coexpansion of sodium vapor of moderate partial pressure (10–100 Torr) together with 2–10 atm argon through a 50-μm nozzle. As described elsewhere,[13] this high seeding ratio provides rotational and vibrational dimer temperatures of 7 and 50 K, respectively. The laser excitation and ionization steps are performed with copper-vapor-laser-pumped homebuilt dye lasers[15] (5 kW, 6 kHz, and 30-ns pulse width). This arrangement provides reasonable mass-selected ion current without saturation of the excitation step.

Among the most important characteristics of the richly structured band system in Fig. 1(b) are the following: (1) A long progression composed of nearly equally spaced bands ($\omega \approx 128$ cm^{-1} or 0.016 eV) appears to be split into *doublets*; (2) a series of closely spaced bands fanning out from the doublet and increasing steadily in breadth accompanies each member of the main progression; (3) a much weaker pattern of levels accounting for all remaining bands fits to a harmonic series with $\omega \approx 137$ cm^{-1}.

These features can be qualitatively understood if one ascribes the following properties to the internal coordinates of the three-body system[15]: The system must be strongly distorted from a (D_{3h}) equilateral triangular configuration, to explain the main progression as a set of transitions to a new equilibrium distance in the distortion-symmetry coordinate (e'). The *direction* (phase) of distortion in this two-dimensional mode must not be strongly preferred, yielding a quasifree internal rotation corresponding to the well-known pseudorotation motion (see Fig. 2), which is required to account for the fanning subpattern associated with each distortion state. The weak progression of 137 cm^{-1} remains to be explained by small-amplitude symmetric vibrations (a_1') of the triangle, negligibly coupled to the distortion and pseudorotation coordinates ρ and ϕ.

A symmetry lowering of this type is predicted for an electronic term which is degenerate at the equilateral configuration, because the electronic wave functions can then be superimposed in an unsymmetrical way, so as to favor distorted configurations (Jahn-Teller theorem[16]). For large distortions and deep states, a simple approximate pattern emerges[9]:

$$E(u,j) = (u+\tfrac{1}{2})\omega_0 + Aj^2, \qquad (1)$$

corresponding to oscillations of the distortion amplitude $(u=0,1,2,\ldots)$ and internal rotation with characteristic rotor constant $A = \hbar^2/2I$. Here $I = m\rho_0^2$ for an X_3 molecule, where m is the mode's reduced mass and ρ_0 is the equilibrium distortion amplitude. If the electronic wave function is required to change sign, then boundary conditions demand $|j| = \frac{1}{2}, \frac{3}{2}, \ldots$. In Fig. 2 the energy-level pattern from this model is given with $\omega_0 = 128$ cm^{-1} and $A = 4$ cm^{-1}. It is readily evident that, although centrifugal terms and localization effects are neglected (see below), only the half-odd spacing accurately reproduces the level pattern. The necessity of half-odd quantum numbers is even more obvious when account of these minor perturbations is made.

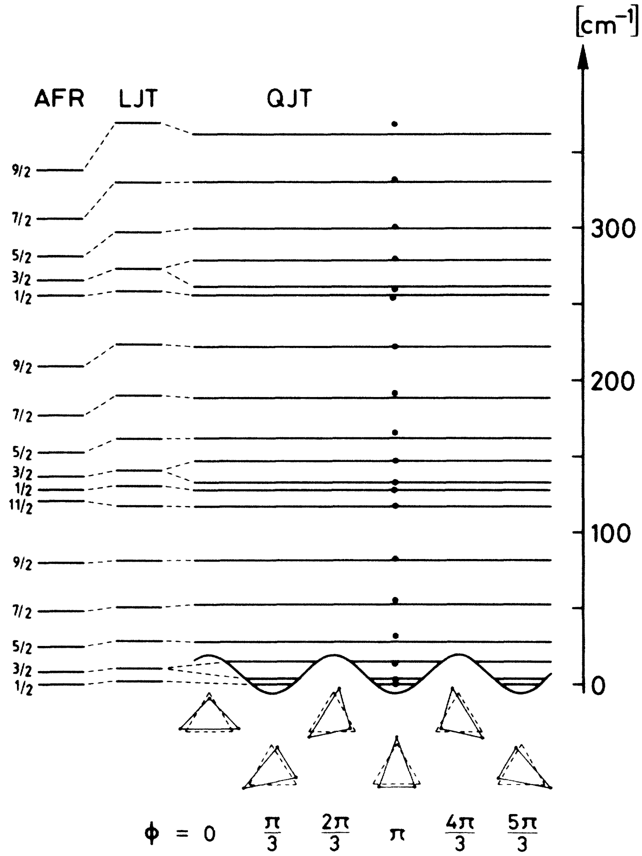

FIG. 2. Comparison of calculated and observed energy levels of $2^2E'$ Na_3. Horizontal lines give calculated values, while points represent observed band maxima. The sinusoidal function gives a cut of the lowest adiabatic surface along the pseudorotation coordinate, and molecular geometries (for arbitrary pseudorotation phase) are given below for surface minima and saddle points. Bond lengths in reduced units are acute 1.14 and 0.76, obtuse 0.91 and 1.24. On the assumption of an equilateral bond distance of 3 Å, apical angles are 39° and 86°, respectively. At left two approximations to the description of this system are given (see text).

A consistent theoretical model of this system, including centrifugal and nonadiabatic effects exactly, can be constructed by a variational solution of the dynamical Jahn-Teller problem. From symmetry alone in a two-state electronic basis $\{|\alpha\rangle, |\beta\rangle\}$, the correct form of the coupling with internuclear motion is (to second order in displacements)[17]

$$\hat{H}=(\hat{T}_N+\tfrac{1}{2}\rho^2)+|\alpha\rangle(k\rho e^{-i\phi}+g\rho^2 e^{2i\phi})\langle\beta|+\text{c.c.} \quad (2)$$

Here $\hat{T}_N$ is the kinetic energy operator of the e' mode, k is the linear Jahn-Teller (distortion) parameter, and g is the quadratic (localization) parameter, in reduced units where $\omega=\hbar=M=1$. Setting $\hat{T}_N=0$ generates adiabatic potential energy surfaces, which for $g=0$ have free internal rotation in a moat of depth $k^2/2$. For g nonzero, a $\cos(3\phi)$ term modulates this motion.[9] Even with neglect of localization ($g=0$), a fit of the spectrum by the simple linear Jahn-Teller model is, but for the splitting of the first excited rotor state of each sequence, essentially quantitative (Fig. 2). All states calculated through the first three rotor sequences fit well the adiabatic separation, $\Psi_e(R)\chi(R)$.

For large distortions, some localization or hindering of the free pseudorotation is expected. The minor remaining discrepancies all fit into the class of effects caused by this localization. When (2) is diagonalized in a basis of 400 functions for the parameters $k=4.04$ and $g=0.012$, the eigenvalue fit indicated in the right-hand side of Fig. 2 is achieved. Quantitative comparison is made in Table I. In this fit, all observed features find a one-to-one correspondence with calculated levels and the typical deviation is only slightly more than the precision of band maxima measurement.

The spectra also convey additional interesting details about this excited state.

(i) Electronic term symmetry.—The ground state of Na_3 is known to be an E' electronic term (united-atom $1P_1$),[18] and, with strong localization in the distortion coordinate, the ground vibronic level is essentially threefold degenerate (E_1', A_2'). If the excited electronic term is E'' then pseudorotation excitations are of (E'', A_2'', A_1'') type, the last of which is rigorously dipole forbidden, so that only one of the two $|j|=\frac{3}{2}$ levels would be visible in each series. However, if the term is E', then spectroscopically allowed (E', A_2', A_1') levels result in agreement with experiment. Because this band system has intensity appropriate to a favored united-atom transition, the excited state must be of D_2 type ($d_{x^2-y^2}, d_{xy}$).[19] It is unlikely that this is a true Rydberg state, but instead it is probably the first excited term of its type: $1D_2$ or $2^2E'$.

(ii) Adiabatic potential energy surface.—The parameters k and g uniquely determine the energy surface in

TABLE I. Energy levels of the $2^2E'$ system of Na_3.

$\nu-\nu_{00}$[a] (cm^{-1})	$(\nu-\nu_{00})/\omega_0$[b]	Calculated[c]	$n(j)$	$\omega_1(a_1')$	Error (cm^{-1})
0	0.00	0.00	0(1/2)		0
2.5	0.02	0.03	0(3/2−)		−1
14.5	0.115	0.13	0(3/2+)		−1.5
32.5	0.255	0.22	0(5/2)		+4
55.0	0.435	0.41	0(7/2)		+2.5
82.5	0.65	0.64	0(9/2 ±)		+1
116.5	0.915	0.92	0(11/2)		−0.5
128	1.01	1.01	1(1/2)		0
133	1.045	1.05	1(3/2−)		−0.5
137	...	...	...	1^1	...
146.5	1.155	1.16	1(3/2+)		−0.5
166.5	1.31	1.27	1(5/2)		+0.5
192.5	1.515	1.48	1(7/2)		+4
222.5	1.75	1.75	1(9/2 ±)		0
	...	1.96	1(11/2)		
254	2.00	2.02	2(1/2)		−2
259.5	2.045	2.06	2(3/2−)		−1.5
270.5	...	...	...	1^2	...
280.5	2.21	2.20	2(3/2+)		+1
301	2.35	2.34	2(5/2)		+1
332	2.615	2.60	2(7/2)		+1.5
369	2.905	2.84	2(9/2 ±)		+6.5
376.5	2.965		3(1/2)		
386.5	3.043		3(3/2−)		
416	3.275				

[a] $\nu_{00}=15\,996$ cm^{-1}.
[b] $\omega_0=127$ cm^{-1}.
[c] With use of Hamiltonian of text [Eq. (2)] with $k=4.04$, $g=0.012$.

the e' coordinate space. For deep states only the lowest adiabatic surface is of interest, which has threefold maxima and minima at $\cos(3\phi) = \pm 1$. Minimizing (2) with respect to ρ for these values gives absolute minima (−) and saddle points (+) at $\rho = k/(1 \pm g)$. For the above parameters, the result is a total stabilization energy of 1050 cm^{-1} and a localization energy of 26 cm^{-1}. A cut of the energy surface at $\rho = k$ is given in Fig. 2. The lowest apparent doublet $(\frac{1}{2}, \frac{3}{2})$ of each j sequence is the result of localization, with a tunneling splitting Δ ranging from 3 to 5 cm^{-1}.

(iii) Real-space description of the pseudorotation.—One expresses the equilibrium distortion ρ_0 in atomic units, $\rho_0 = (\hbar/m\omega_0)^{1/2}k$, where for X_3 systems $m = (3M_X)^{1/2} = 8.3$ amu, and $\rho_0 = 0.71$ Å. The displacement amplitude r_i of each atom is therefore $r_i = \rho_0/\sqrt{3} = 0.41$ Å from the equilateral configuration (see Fig. 2).[15]

(iv) Coriolis coupling.—Large-amplitude internal motion implies a nonnegligible coupling with rotation about the center of mass. Accordingly, note that the individual bands have widths increasing linearly with j, the pseudorotation quantum number. Such behavior is the hallmark of the Coriolis effect, which here involves the transformation of the pseudorotation angular momentum into the frame of the molecule rotating with rotation constant B about its center of mass in the plane. Analysis, neglecting centrifugal effects, predicts a K splitting of $4BjK$. This splitting yields precisely the observed pattern if K states are weighted according to $T_{rot} = 10$ K. Broader envelopes at higher temperature account for the loss of pseudorotation structure in less-efficient expansions.[20]

To summarize, the resulting picture of excited Na_3 (Fig. 2) is that of a molecule undergoing slow, weakly hindered internal rotation accompanied by electronic-state evolution such that the electronic wave function, best represented by D_2 orbitals, changes sign upon each complete internal rotation.[8] We have demonstrated the necessity of fractional quantization of this motion. High-resolution experiments will provide better tests of fractional quantization and will also directly verify the proposed Coriolis coupling mechanism. With short laser pulses ($\tau < \Delta^{-1}$) it may be possible to prepare states with a specified quantum phase and observe their temporal evolution directly. We also mention that for large atomic clusters new quantum phases may be found.[10]

This research has benefitted from discussions with G. S. Ezra, D. Lindsay, J. Gole, M. Broyer, M. V. Berry, Ch. Jungen, and K. S. Haber. Two of us (E.R.G.) and (J.W.Z.) acknowledge support through a grant from the U.S. National Science Foundation. One of us (R.L.W.) was the recipient of a Dreyfus Distinguished New Faculty Award.

Note added.—Since this work was completed, Moody, Shapere, and Wilczek[21] have presented specific candidates for experimental detection of $\gamma_n(c)$ in molecular systems, which are unrelated to the present example.

[1]T. Kato, J. Phys. Soc. Jpn. **5**, 435 (1950); M. Born and V. Fock, Z. Phys. **51**, 165 (1928).

[2]M. V. Berry, Proc. Roy. Soc. London, Ser. A **392**, 45 (1984); see also J. H. Hannay, J. Phys. A **18**, 221 (1985); M. V. Berry, J. Phys. A **18**, 15 (1985); C. A. Mead and D. G. Truhlar, J. Chem. Phys. **70**, 2284 (1979).

[3]H. Kuratsuji and S. Iida, Prog. Theor. Phys. **74**, 439 (1985); H. Kuratsuji and S. Iida, Phys. Rev. Lett. **56**, 1003 (1986).

[4]B. Simon, Phys. Rev. Lett. **51**, 2164 (1983).

[5]D. Arovas, J. R. Schrieffer, and F. Wilczek, Phys. Rev. Lett. **53**, 722 (1984).

[6]J. R. Schrieffer, Mol. Cryst. Liq. Cryst. **118**, 57–64 (1985).

[7]F. Wilczek and A. Zee, Phys. Rev. Lett. **52**, 2111 (1984).

[8]G. Herzberg and H. C. Longuet-Higgins, Discuss. Faraday Soc. **35**, 77 (1963); H. C. Longuet-Higgins, Proc. Roy. Soc. London, Ser. A **344**, 147 (1975).

[9]H. C. Longuet-Higgins, Adv. Spectrosc. **2**, 429 (1961).

[10]S. P. Keating and C. A. Mead, J. Chem. Phys. **82**, 5102 (1985), and references within.

[11]C. A. Mead, Chem. Phys. **49**, 23 (1980).

[12]A. Herrmann, M. Hoffmann, S. Leutwyler, E. Schumacher, and L. Wöste, Chem. Phys. Lett. **62**, 216 (1979).

[13]G. Delacrétaz, G. D. Stein, and L. Wöste, to be published.

[14]G. Delacrétaz and L. Wöste, Surf. Sci. **156**, 770 (1985).

[15]M. Broyer, J. Chevaleyre, G. Delacrétaz, and L. Wöste, Appl. Phys. B **35**, 31 (1984).

[16]T. C. Thompson, D. G. Truhlar, and C. A. Mead, J. Chem. Phys. **82**, 2392 (1985).

[17]H. A. Jahn and E. Teller, Proc. Roy. Soc. London, Ser. A **161**, 220 (1937).

[18]D. M. Lindsay and G. A. Thompson, J. Chem. Phys. **77**, 1114 (1982); R. L. Martin and E. R. Davidson, Mol. Phys. **35**, 1713 (1978); J. L. Martins, R. Car, and J. Buttet, J. Chem. Phys. **78**, 5646 (1983).

[19]We adopt for Na_3 the ordering of excited states of W. D. Knight *et al.*, Phys. Rev. Lett. **52**, 2141 (1984). The Na_3 ground term is therefore $^2P_1$, where the splitting of the $P_{|1|}$ and P_0 orbitals is noted. This ordering is also given by W. Gerber, Ph.D. thesis, Universität Berne, 1981 (unpublished), without the united-atom labels used here.

[20]H. P. Härri, Ph.D. thesis, Universität Berne, 1983 (unpublished).

[21]J. Moody, A. Shapere, and F. Wilczek, Phys. Rev. Lett. **56**, 893 (1986).