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A Complete Experimental Assessment of Franck–Condon Structural Effects for an Irreversible Outer-Sphere Electron-Transfer Reaction: Applications of Time-Dependent Raman Scattering Theory to the One-Electron Reduction of 4-Cyano-*N*-methylpyridinium

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A complete experimental description of the vibrational Franck–Condon barrier to the one-electron reduction of 4-cyano-*N*-methylpyridinium cation (NC-py-CH_3^+) has been obtained. Because of the chemical irreversibility of the electron transfer, the reaction is not readily amenable to study by conventional structural methods. The approach successfully employed here, however, was a time-dependent analysis of near-resonant Raman scattering where resonance was achieved by pairing the cation to iodide anion; the pairing gives rise to a weak (ϵ = 565 M^{-1} cm^{-1}) outer-sphere charge-transfer band centered at 428 nm in acetonitrile as solvent. The time-dependent analysis of scattering yields vibrational frequencies, coordinate displacements, and single-mode barrier contributions for each of 13 modes involved in outer-sphere electron transfer. Depolarization measurements, excitation profiles, and scattering studies with the nonchromophoric [NC-py-CH_3^+,Cl^-] ion pair confirm that the vibrational structural data pertain directly to the outer-sphere charge-transfer reaction rather than to higher lying electronic transitions.

TABLE I: Structural and Franck–Condon Charge-Transfer Parameters for Resonance-Enhanced Raman Scattering from 4-Cyano-*N*-methylpyridinium Iodide

freq,[a] cm^{-1}	rel intensity[e]	Δ^2[f]	χ_i',[g] cm^{-1}	assignment[h,i]
2250[b]	0.37	0.17	192	$\nu(C{\equiv}N)$
1650	1.00	0.87	717	$\nu(C{=}C)$
1490[c,d]	0.25	0.27	198	$\delta_{as}(CH_3)$
1290[d]	0.20	0.29	188	$\nu(N^+–CH_3)$
1234[d]	0.38	0.60	368	$\nu(C{=}N^+CH_3)$
1213	0.32	0.52	314	δ(C–H)(ring)
1182	0.99	1.70	1000	ring breathing or δ(C–H)(ring)
844	0.42	1.44	608	δ(C–H)(ring)
724	0.03	0.16	57	γ(C–H)(ring)
678	0.08	0.43	147	γ(C–H)(ring)
590[d]	0.12	0.85	250	$\gamma(C{=}N^+{—}CH_3)$
551	0.15	1.22	337	$\delta(C{=}N^+{=}C)$
416[c,d]	0.19	2.62	545	$\gamma(CH_3)$

[a] Determined in acetonitrile as solvent, except as noted. [b] Determined in acetone as solvent. [c] Determined in acetonitrile-d_3 as solvent. [d] Mode is extensively shifted or absent in [NC-py-CD_3^+,I^-]. [e] Intensities are corrected for sample self-absorption (Shriver, D. F.; Dunn, J. B. R. *Appl. Spectrosc.* **1974**, *28*, 319), spectrometer throughput, and detector response. [f] Unitless normal-coordinate displacement squared, calculated from eqs 3 and 4 as indicated in text, with σ = 2460 ± 10 cm^{-1}. [g] Single-mode contribution to total vibrational (Franck–Condon) reorganization energy; obtained as indicated in text. [h] Abbreviations are as follows: ν = stretch, δ = out-of-plane (C–H) or out-of-phase (CH_3) bend, γ = in-plane bend, as = asymmetric. [i] Preliminary mode assignments made on the basis of isotopic substitution (see above) and comparison with literature reports (ref 16).

Activation barrier heights, and therefore rates, for molecule-based electron-transfer (ET) reactions are governed by redox thermodynamics and by Franck–Condon effects.[1] Quantitative assessment of the latter requires a detailed, quantitative knowledge of all internal and external normal-coordinate displacements, together with appropriate vibrational frequencies (ν) or force constants. In favorable cases, the desired internal or vibrational displacement information can be satisfactorily estimated from redox-induced bond length changes as provided, for example, by X-ray crystallography or EXAFS measurements.[2,3] There are, however, a number of limitations.[4] We have recently shown[5-8] that an attractive alternative to the X-ray approach is the direct assessment of coordinate displacement parameters via a time-dependent analysis[9-11] of resonance Raman scattering spectra. To date, the Raman approach has been successfully applied to metal-to-ligand,[5] metal-to-metal,[6] and metal-to-surface[7] charge-transition reactions. Interestingly, in each of these cases important redox structural data have been obtained which, in retrospect, could not have been uncovered by traditional X-ray methods (although X-ray results have been used to corroborate some of the more significant Raman-generated structural findings).[5-7] In each of the prior studies[5-7] ET has involved covalently linked or bridged donors and acceptors. While these "inner-sphere" reactions are important, they comprise but a small fraction of the known inorganic, organic, and biological redox reactions. We now wish to report the first successful application of the Raman methodology to a much larger class of ET reactions, namely, outer-sphere reactions. The report also necessarily represents the

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(1) General reviews: (a) Sutin, N.; Newton, M. D. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437. (b) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (c) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(2) See, for example: Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1983**, *87*, 3360.

(3) Other potentially useful methods include Franck–Condon analysis of structured emission or absorption spectra, hole-burning techniques, and application of empirical structure/frequency relationships (e.g. Badger's rules).

(4) For a brief discussion, see ref 5. The most obvious limitations for crystallography are that measurements can be made only in a crystalline environment and that experiments cannot be done on short-lived electron-transfer excited states or on systems which suffer from chemical decomposition following oxidation or reduction. For EXAFS there are additional constraints in that only selected elements display useful scattering and only atoms in close proximity to the scattering center may be detected.

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(6) Doorn, S. K.; Hupp, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 1142.

(7) Blackbourn, R. L.; Johnson, C. S.; Hupp, J. T. *J. Am. Chem. Soc.* **1991**, *113*, 1060.

(8) See also: Doorn, S. K.; Hupp, J. T.; Porterfield, D. R.; Campion, A.; Chase, D. B. *J. Am. Chem. Soc.* **1990**, *112*, 4999.

(9) (a) Heller, E. J.; Sundberg, R. L.; Tannor, D. *J. Phys. Chem.* **1982**, *86*, 1822. (b) Tannon, D.; Heller, E. J. *J. Chem. Phys.* **1982**, *77*, 202. (c) Lee, S. Y.; Heller, E. J. *J. Chem. Phys.* **1977**, *71*, 4777. (d) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 368.

(10) See also: (a) Warshel, A.; Dauber, P. *J. Chem. Phys.* **1977**, *66*, 5477. (b) Myers, A. B.; Mathies, R. A. In *Biological Applications of Raman Spectroscopy*; Spiro, T. G., Ed.; John Wiley and Sons: New York, 1987; Vol. 2. (c) Schomacker, K. T.; Bangcharoenpaurpong, O.; Champion, P. M. *J. Chem. Phys.* **1984**, *80*, 4701. (d) Hizhnyakov, V.; Tehver, I. *J. Raman Spectrosc.* **1988**, *19*, 383. (e) Page, J. B.; Tonks, D. L. *Chem. Phys. Lett.* **1979**, *66*, 449. (f) Morris, D. E.; Woodruff, W. H. *J. Phys. Chem.* **1985**, *89*, 5795.

(11) Related experimental applications of time-dependent Raman scattering theory: (a) Tutt, L.; Zink, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 5830. (b) Zink, J. I.; Tutt, L.; Yang, Y. Y. *ACS Symp. Ser.* **1986**, *No. 307*, 39. (c) Zink, J. I.; Shin, K.-S. K. In *Advances in Photochemistry*; Volman, D. H., Hammond, G. S., Neckers, D. C., Eds.; John Wiley and Sons: New York, 1991; Vol. 16.

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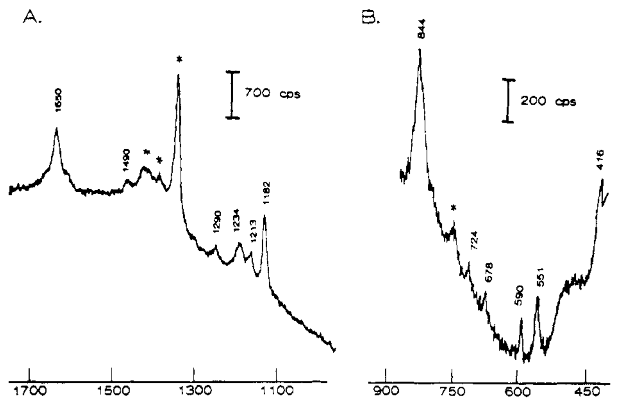
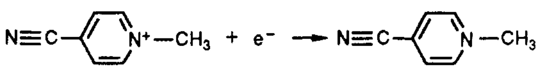


Figure 1. Near-resonant Raman scattering spectrum (514.5-nm excitation) of [NC-py-CH_3^+,I^-] in acetonitrile: (A) 50 mM chromophore; (B) 100 mM chromophore. Solvent peaks are indicated by asterisks. (Note that the sloping background is due to an impurity fluorescence.)

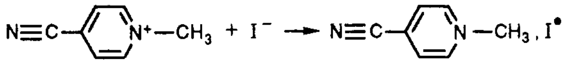
first application to a "monomeric" redox system.

The specific reaction we have examined is the one-electron reduction of 4-cyano-*N*-methylpyridinium:[12,13]



(1)

To provide electronic and vibrational spectroscopic access, the 4-cyano-*N*-methylpyridinium cation (NC-py-CH_3^+) was paired with iodide anion in acetonitrile as solvent. Because iodide is an excellent electron donor, the pairing gives rise to an outer-sphere charge-transfer absorption band, centered at 428 nm (ϵ = 565 M^{-1} cm^{-1}):[14]



(2)

We note further that because the iodide ion is monatomic, all vibrational spectroscopic information necessarily pertains exclusively to the NC-py-$CH_3^{+/0}$ redox couple.

Figure 1 shows a Raman spectrum of [NC-py-CH_3^+,I^-] based on near-resonant excitation (514.5 nm).[15] Preliminary analysis indicates that at least 13 modes are active. Table I gives a listing along with preliminary assignments.[16] Two experiments were done to show that the scattering is resonantly enhanced: (1) Spectra were recorded off resonance (647.1-nm excitation) and were found to be greatly diminished in intensity. (2) At 514.5 nm, spectra were recorded for both [CN-py-CH_3^+,Cl^-] and [CN-py-CH_3^+,I^-] (Figure 2).[17] The former is nonchromophoric at this wavelength due to the comparatively poor electron-donating ability of chloride. As expected, scattering from the chloride salt is considerably diminished. Both experiments indicate, in fact, that all of the modes listed in Table I are electronically enhanced and that the enhancements amount to factors of 5 or more. Nevertheless, in view of the very weak extinction for eq 2, and to confirm that enhancement comes solely from Condon sources, we additionally measured the following: (3) depolarization ratios, which indicated that all modes are totally symmetric,[18] and (4) excitation profiles[19] (406.7, 441.5, 457.9, 476.5, 488.0, 496.5, 514.5, 530.8, and 647.1 nm) which permitted us to rule out coupling to higher excited states as a major enhancement mechanism.[20]

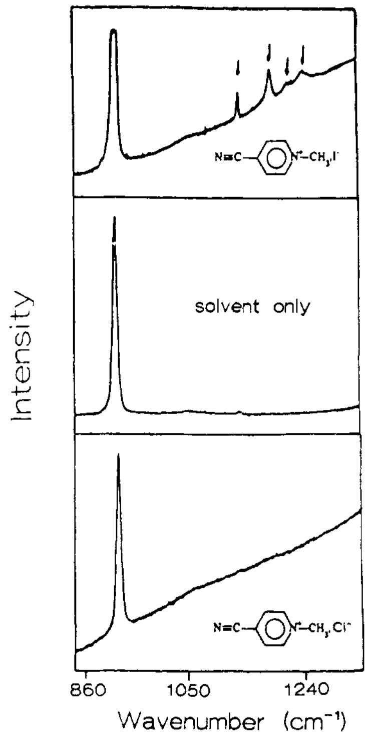


Figure 2. Raman spectra for 4-cyano-*N*-methylpyridinium iodide in acetonitrile (top), acetonitrile only (middle), and 4-cyano-*N*-methylpyridinium chloride (bottom). Excitation wavelength = 514.5 nm. Resonantly enhanced peaks (top spectrum) are labeled with arrows. (The large peak on the left-hand side of each spectrum is due to a reference compound.)

To relate the Raman spectra to the desired Franck–Condon structural parameters, we have made use of the following simplified intensity relationships:[21-23]

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(12) 4-Cyano-*N*-methylpyridinium iodide was prepared from reagent grade 4-cyanopyridine (Aldrich) and methyl iodide (Aldrich) in absolute ethanol following the general method of Kosower and Klinedinst (*J. Am. Chem. Soc.* **1956**, *78*, 3493). The crude yellow product was recrystallized from ethanol. [NC-py-CD_3^+,I^-] was similarly made by using CD_3I. The nonchromophoric chloride salt was prepared by stepwise metathesis, first with NH_4PF_6 in water and then with tetrabutylammonium chloride in acetone to yield a white solid.

(13) NC-py-CH_3^+ and related ions have found extensive application as electron-transfer quenchers in fundamental kinetic studies of molecular excited-state reactivity. Representative reports: (a) Marshall, J. L.; Stobart, S. R.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 3027. (b) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790.

(14) The absorption band energy is in agreement with Kosower (*J. Am. Chem. Soc.* **1958**, *80*, 3253). The concentration-dependent extinction coefficient (ϵ) was determined in a 50 mM solution with a 0.01 cm path length cell.

(15) The laser sources for sample excitation at 514.5 and 647.1 nm consisted of Spectra Physics Series 2000 Ar^+ and Kr^+ lasers, respectively. An RCA C31034A photon counting tube was used in conjunction with a Spex 1401 double monochromator to collect the time-averaged Raman spectra. Typical band-pass was 5 cm^{-1}. Scattered light was collected in a 180° backscattering geometry and focused onto the monochromator entrance slit with the aid of a 35-mm camera lens. The samples were dissolved in distilled, dry acetonitrile and irradiated in a spinning NMR tube.

(16) Pertinent references include: (a) Foster, M.; Girling, R. B.; Hester, R. E. *J. Raman Spectrosc.* **1982**, *12*, 36. (b) Spinner, E. *Aust. J. Chem.* **1967**, *20*, 1805. (c) Cyr, A.; Laviron, E.; Lessard, J. *J. Electroanal. Chem.* **1989**, *263*, 69. (d) Datta, M.; Jansson, R. E.; Freeman, J. J. *Appl. Spectrosc.* **1986**, *40*, 251. (e) Lee, P. C.; Schmidt, K.; Gordon, S.; Meisel, D. *Chem. Phys. Lett.* **1981**, *80*, 242. (f) Hester, R. E.; Suzuki, S. *J. Phys. Chem.* **1982**, *86*, 4626. (g) Blatter-Mörke, I.; von Känel, H.; Wachter, P. *J. Phys. Chem.* **1987**, *91*, 553. (h) Benchenane, A.; Bernard, L.; Theophanides, T. *J. Raman Spectrosc.* **1974**, *2*, 543. (i) Spinner, E. *J. Chem. Soc.* **1963**, 3860. (j) Cook, D. *Can. J. Chem.* **1961**, *39*, 2009.

(17) Raman spectra (Arizona) were acquired using 514.5-nm laser excitation from a Coherent Innova 90-5 Ar^+ laser. Scattered radiation was collected with a Minolta *f*/1.2 lens and focused onto the slits of a Spex Triplemate spectrometer. Detection was accomplished with a Photometrics PM 512 CCD cooled to −110 °C. The camera system was a Photometrics RDS2000 system with a custom version of Spectracalc.

(18) The appearance of nontotally symmetric modes would have signaled the occurrence of undesired "*B* term" scattering (i.e., Herzberg–Teller coupling to higher electronic excited states). We note that the simplified time-dependent analysis is applicable only to Albrecht *A* term scattering.[9]

(19) A Coherent Innova 100 Kr^+ laser (Marquette University) provided sample excitation at 406.7 and 530.8 nm. Excitation at 441.5 nm was accomplished with a Liconix He:Cd laser, Model 4240NB. Dispersion of the scattered light was achieved by using a Spex Model 1403 double monochromator equipped with a Hamamatsa Model R928 photomultiplier tube. A Spex DM1B was used for the data analysis.

(20) The excitation profile experiments provide additional evidence that scattering occurs by an *A* term, rather than *B* term, mechanism. For constructive *B* term scattering (destructive effects are also possible) the Raman intensity should vary roughly as $(\nu_2 - \nu_{exc})^{-2}$, rather than $(\nu_1 - \nu_{exc})^{-2}$, where ν_{exc} is the excitation frequency, ν_2 is the frequency for the ground to second excited state transition, and ν_1 is the frequency for the ground to first excited state transition. We note that, for [NC-py-CH_3^+,I^-] as the chromophore, the next higher excited state (which is also charge transfer in nature) lies approximately 9500 cm^{-1} above the resonant charge-transfer state (eq 2) examined here. See, for example: Mackay, R. A.; Landolph, J. R.; Poziomek, E. J. *J. Am. Chem. Soc.* **1971**, *93*, 5026.

$$I_1/I_2 = \Delta_1{}^2\nu_1{}^2/\Delta_2{}^2\nu_2{}^2 \qquad (3)$$

$$2\sigma^2 = \sum_k \Delta_k{}^2\nu_k{}^2 \qquad (4)$$

In eqs 3 and 4, I_1 and I_2 are relative scattering intensities, Δ is a unitless normal-coordinate displacement, $8\sigma^2$ is the square of the electronic absorption bandwidth at $1/e$ of the height,[22] and the summation is over all enhanced modes that show significant intensity in the spectrum. Table I lists the resulting displacement data. Also listed are single-mode contributions, χ_i' ($=0.5\ \Delta^2\nu$), to the total redox-induced vibrational reorganization energy.[23]

Perhaps the most significant finding (besides the observation that enhanced scattering can be observed at all, from such a weak transition) is that a very large number of modes participate in the ET process. Unfortunately, in the absence of an appropriate force field and normal-coordinate analysis it is impossible to relate the displacements directly to bond length changes; the assignments in Table I, therefore, should be viewed as predominant, rather than exclusive, structural motions. It is worth recalling, however, that normal-coordinate (rather than local coordinate or bond length) displacements are, in fact, the fundamental parameters required by most contemporary ET theories.[1] Finally, it is worth noting that in most solvents NC-py-$CH_3{}^+$ reduction is *chemically* irreversible on a time scale of minutes to seconds.[24] (Product decomposition evidently occurs by a dimerization pathway.[25]) This renders structural studies by conventional X-ray methods impossible, leaving Raman scattering as perhaps the only viable experimental methodology. We are optimistic that the technique can be generalized to yield in situ structural information for a range of interesting outer-sphere ET reactions.

Acknowledgment. We thank Dr. Gerry Danzer and Prof. Jim Kincaid of Marquette University for assistance and use of equipment in some of the excitation profile studies. The research at Northwestern was supported by the U.S. Department of Energy, Office of Energy Research, Division of Chemical Sciences (Grant DE-FG02-87ER 13808), and at Arizona by the National Science Foundation (Grant CHE-8614955). A portion of the Raman instrumentation at Northwestern is maintained by the Materials Research Center (Grant NSF-DMR-8821571). The remaining instrumentation at NU was acquired with the generous assistance of the Department of Energy and the Northwestern University Research Grants Committee. J.T.H. acknowledges an Alfred P. Sloan Foundation Fellowship and a Dreyfus Teacher-Scholar Award. Finally, we thank Prof. Anne Myers for a copy of a preprint cited in ref 22.

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(21) The most important simplifying assumptions made in the derivation of eq 3 are (1) that mode mixing in the excited state (Duschinsky rotation) is absent, (2) that Herzberg-Teller coupling is absent, (3) that only a single electronic transition is in resonance or near resonance, (4) that only ground vibrational states of the ground electronic state are populated, and (5) that scattering occurs under "short time" conditions. Assumptions 2, 3, and 5 have been confirmed for the present system via excitation profile studies (see text). At room temperature, (4) is expected to hold for all of the modes contained in Table I (see ref 10c for further discussion). On the other hand, assumption 1 quite possibly does not fully hold. Usable theory is available to handle this more complex case (see ref 10f). Unfortunately, the required input data (vibrational frequencies for the charge-transfer photoproduct) are not.

(22) Equation 4 assumes that the entire absorption line width may be ascribed to vibrational Franck-Condon effects. Other potential sources of width are inhomogeneity effects, solvent reorganization, and very low frequency *inter*molecular modes. The first can probably safely be neglected for this simple ion pair in polar liquid environments. The second we have assumed is small. If so, then it will serve to broaden the individual vibrational components but will not appreciably affect the *overall* line width. If it is not small, then some broadening obviously will occur and the direct use of eq 4 will lead proportionally to overestimates in both Δ^2 and χ_i'. The third source of broadening, if present, could also lead to overestimates in reorganizational parameters. Precedents do exist in Raman studies for detectable intermolecular donor-acceptor modes. (See, for example: McHale, J. L.; Merriam, M. J. *J. Phys. Chem.* **1989**, *93*, 56. Markel, F.; Ferris, N. S.; Gould, I. R.; Myers, A. B. Manuscript submitted.) Unfortunately, with existing instrumentation at NU we have been unable to explore adequately the low and very low frequency vibrational region.

(23) A reviewer has suggested that we compare our results for the vibrational activation barrier to those which might be expected based on an analysis of bimolecular ET self-exchange kinetics. Unfortunately, despite ref 13 and several related reports, we have been unable to find an experimental measurement or estimate for the NC-py-$CH_3{}^{+/0}$ self-exchange rate. Nevertheless, for the self-exchange we may approximate the classical vibrational activation barrier height ($\Delta G_{\mathrm{vib}}{}^*$) as one-fourth the internal reorganization energy, which, in turn, is *twice* the sum of the χ_i values in Table I (because two redox centers must be activated). On this basis we find $\Delta G_{\mathrm{vib}}{}^* = 2460\ \mathrm{cm}^{-1}$ (7 kcal mol^{-1}). Note, however, that at room temperature modes of higher frequency will be difficult to activate and will likely remain frozen (i.e., displaced only by tunneling processes). If, for simplicity, we regard all modes above $4kT$ (828 cm^{-1}) as entirely frozen and all modes below $4kT$ as fully classical, we obtain an effective thermal barrier height (vibrations only) of just 670 cm^{-1} (1.9 kcal mol^{-1}). A barrier of this height would attenuate the self-exchange kinetics by only about a factor of 25. If a frequency factor of 10^{12} s^{-1} is assumed, with a precursor formation constant of 0.1 M^{-1}, no work terms, and a solvent activation barrier given by the simple Marcus model (two spheres; $r \approx 5$–7 Å, $d = 2r$), then a very crude estimate for the overall self-exchange rate constant (CH_3CN as solvent) would be 3×10^7–2×10^9 M^{-1} s^{-1}.

(24) We have additionally assumed that the extent of ground-state charge transfer between NC-py-$CH_3{}^+$ and I^- is small. To the extent that this is *not* the case, the degree of reduction experienced by the 4-cyano-*N*-methylpyridinium in the photoreaction (eq 2) will be less than in the isolated thermal process (eq 1). Raman experiments would then presumably provide only lower limit estimates for the magnitudes of displacements encountered in the latter process.

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Endohedral Vibrations of Na^+ in C_{60}

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We report the results of a theoretical investigation of the possible vibrations of a single sodium cation trapped inside C_{60}. To begin, all-electron local density functional (LDF) calculations provided the total energy of the $C_{60}Na^+$ species with respect to the displacement of the ion along the internal C_{3v} and C_{5v} symmetry axes. Consistent with other calculations, we found the positions of equilibrium displaced from the center; thus, tunneling is possible between positions of equilibrium. To analyze this situation, a pair potential for the interaction between the ion and the individual carbon atoms was fit to the LDF-determined energies. A completely anharmonic variational analysis that accounts for the delocalization via tunneling of the ion inside the sphere was used to determine the fundamental frequencies. Clusters of infrared (dipole) active transitions over a wide range of frequencies were found.

Introduction

The carbon allotrope C_{60}, now better known as *buckminsterfullerene* or *buckyball*, has captured considerable attention.[1,2] New synthetic methods[2] now yield sufficient amounts of this unusual substance for regular chemical and physical examination, some of which has already been done. Nevertheless, many of the

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(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 163.

(2) Krätschmer, W.; Lamb, L. D.; Fostiropolous, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.