PHYSICAL REVIEW B VOLUME 49, NUMBER 18 1 MAY 1994-II

Temperature dependence of the proton hyperfine interaction in HC_{60} and the proton-muon hyperfine anomaly

J. R. Morton, F. Negri,* and K. F. Preston
Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

(Received 26 October 1993; revised manuscript received 13 December 1993)

The decrease in the proton hyperfine interaction of HC_{60} with increasing temperature is analyzed on the basis of quantum-chemical calculations of the vibrational force field of the radical. The changes of the hyperfine interaction with respect to normal-mode displacements are evaluated and used to simulate the temperature dependence. It is shown that the modulation by low-frequency A'' (C_s symmetry) vibrational modes of the radical that correspond to the lowest h_g and h_u vibrations of C_{60} dominates the observed temperature dependence. The experimentally observed negative hyperfine anomaly, vis-à-vis the muon coupling, is also attributed to vibrational motions, specifically to the three modes that describe hydrogen motions.

A natural consequence of our discovery of the EPR spectra of alkyl-C_{60} radicals[1] was a search for the prototype, HC_{60}. This species is important for three reasons: (i) it is possibly a constituent of interstellar space;[2,3] (ii) its ^1H and ^{13}C hyperfine interactions (a_H and a_C) will provide templates against which to assess the various theoretical calculations of spin-polarization phenomena; [4-10] and (iii) the ratio of its proton hyperfine interaction (hfi) to that of the muon[4,11,12] in MuC_{60} is anomalous.[3] In this work we report the measurement of the temperature coefficient of a_H, and we analyze its origin and that of the Mu-H hyperfine anomaly on the basis of quantum-chemical calculations of the vibrational normal modes of HC_{60} and MuC_{60}.

The EPR spectrum of HC_{60} can be generated by the UV photolysis of a 0.0005-M solution of C_{60} in toluene containing benzophenone (0.001 M) and isopropanol (0.5 M). The photolytically induced reaction sequence is presumably[13]

$$(C_6H_5)_2CO + h\nu \rightarrow (C_6H_5)_2CO^* ,$$

$$(C_6H_5)_2CO^* + (CH_3)_2CHOH \rightarrow (C_6H_5)_2COH + (CH_3)_2COH ,$$

$$(CH_3)_2COH \rightarrow (CH_3)_2CO + H ,$$

$$(C_6H_5)_2COH \rightarrow (C_6H_5)_2CO + H ,$$

$$H + C_{60} \rightarrow HC_{60} .$$

The samples were prepared in a glove box continuously flushed with dry argon, using C_{60} obtained from Strem Chemical Corp (Newburyport, MA) and other chemicals from Aldrich Chemicals Inc. (Milwaukee, WI). The sample was photolyzed in the cavity of the EPR spectrometer using the focused light of a Schoeffel 1000 W Hg/Xe arc. A 5-cm water filter and an Oriel IR filter were used to prevent drift of the microwave frequency. The spectrometer and ancilliary equipment have been adequately described elsewhere.[14] The individual lines in the spectrum of HC_{60} were extremely sharp ($\Delta B_{ms} \simeq 0.05$ G), and care had to be taken not to modulation or saturation broaden them. The best operating conditions were microwave power 0.05 mW, magnetic-field modulation 25 kHz, 0.05 G. The resonant magnetic fields and microwave frequencies were converted to the g factor and proton hfi of HC_{60} using a computer program appropriate for the exact solution of an isotropic Hamiltonian.

The EPR spectrum of HC_{60} at 295 K consists of a pair of transitions separated by about 33 G. A curious feature of the spectrum is that the low-field line is emissive (E) and the high-field line absorptive (A). Such behavior is due to chemically induced dynamic electron polarization (CIDEP) originating with pairs of radicals.[15,16] The hfi and g factor of HC_{60} were measured as accurately as possible over the temperature range 240–400 K. Below 240 K the spectrum could no longer be detected. Within experimental error, the proton hfi was a linear function of temperature for the range covered [Fig. 1(a)]. Least-squares procedures provided the best-fit parameters to the function $a(T) = a_0 + b_1 T$:

$$a_0 = 94220 \pm 40 \text{ kHz} , \tag{1}$$

$$b_1 = -4.25 \pm 0.14 \text{ kHz/deg} . \tag{2}$$

The g factor of 2.00209 ± 0.00005 was temperature independent.

The vibrational force field and normal modes of HC_{60} and MuC_{60} were obtained by employing an updated version[17] of the quantum-consistent-force-field–π-electron (QCFF-PI) method[18] that can describe electronic states of any spin multiplicity. This Hamiltonian has been shown to successfully predict the vibrational frequencies of C_{60},[19] C_{70},[20] and C_{60}^{6-}.[21] The force field discussed in this work was computed at the equilibrium geometry of the HC_{60} radical, obtained as described in detail elsewhere.[6] Addition of a hydrogen atom to C_{60} will result in three vibrational modes describing H motion, and 174 modes derived from C_{60}. In the following we will refer to the latter as C_{60}-like vibrational modes. The moderate geometrical distortion induced by the addition of a hydrogen atom does not alter significantly the vibrational frequencies of the C_{60} framework, which remain very close to those of the unperturbed C_{60}. However, splittings arise due to symmetry lowering. Among the three additional frequencies describing the hydrogen motion, the CH stretch falls in a frequency region (~ 2993 cm^{-1}) where no other fundamental is calculated, while the two CCH bends, as expected, have frequencies (~ 1160 and 1290 cm^{-1}) very close to a number of CC stretches and CCC deformations of the cage. As a consequence, strong mixing occurs among these modes, as analysis of the Dushinsky rotation[22] between the normal coordinates of C_{60} and HC_{60} indicates. Of particular interest to us is the CH wagging which belongs to the A'' representation of C_s symmetry. Inspection of the Dushinsky coefficients shows that, of the two CCH bends, the wagging undergoes the largest mixing with C_{60}-like normal modes. In particular, the largest CH wagging components are calculated for the 1156- and 1168-cm^{-1} fundamentals. We are led to the same conclusion by the analysis of the normal-mode rotation (Dushinsky mixing) of the HC_{60} and MuC_{60} vibrational coordinates: the A'' CMu wagging, calculated at 3351 cm^{-1}, in a frequency region well separated from C_{60}-like fundamentals, correlates with both the 1156- and 1168-cm^{-1} frequencies of the protonated radical, the first of these showing the largest coefficient. The mode-mixing analysis also confirms that the 3748-cm^{-1} rocking and the 8800-cm^{-1} stretch modes of the muonated radical correspond to the 1294- and 2993-cm^{-1} frequencies of HC_{60}.

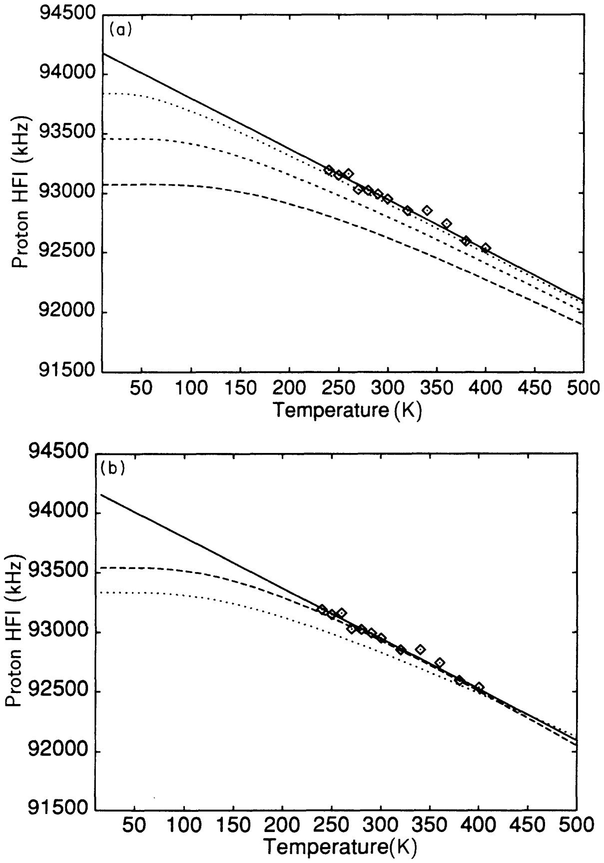

FIG. 1. Observed and computed temperature dependence of the isotropic ^1H hyperfine interaction in HC_{60}: least-squares best fit (solid line) to the experimental data in liquid toluene (diamonds) and curves computed (a) using the *one-mode* model with vibrational frequencies of 125 cm^{-1} (dotted line), 250 cm^{-1} (dashed line), and 375 cm^{-1} (long-dashed line); (b) using the *multimode* model; (dotted line) simulation with b_1^i parameters computed for all the vibrational normal modes and $a_0' = 92\,700$ kHz; (long-dashed line) the b_1^i parameters of the 70 lowest-frequency modes were scaled by 1.2 and $a_0' = 93\,250$ kHz (see discussion in the text).

To evaluate the effect of the molecular vibrations on the proton hfi we have calculated the numerical second derivatives of the hfi with respect to each normal coordinate Q_i of the radical. In fact, we have computed the second derivatives of the 1*s* spin population of the hydrogen atom by using the MNDO Hamiltonian[23] within the half-electron (HE) scheme,[24] followed by configuration interaction (CI) as described in Ref. 6. To obtain the hfi derivatives we multiply the spin-density derivatives by a constant A deduced from the ratio of the observed hydrogen hfi (93350 kHz) with the calculated 1*s* spin population obtained at the equilibrium geometry of the radical. Since at the QCFF-PI optimized geometry the MNDO Hamiltonian predicted spin density on the hydrogen to be 0.0211,[6] we obtain a value of 4 424 171 kHz for the constant A. We are conscious of the underestimate of MNDO spin populations by a factor of ~ 3 in the He+CI scheme; however, as pointed out in Ref. 6 we believe that this discrepancy can be corrected by scaling the computed spin densities. In fact, we have recently shown that, although the absolute magnitude is underestimated, the ratio of spin populations computed for protons in various H_nC_{60} derivatives reproduces very well the ratio of the observed hfi's.[6]

A linear decrease in the Mu hfi with temperature has also been observed[12] for the muonated radical MuC_{60} in the quasifree-rotator phase of solid C_{60} (above 260 K). The temperature coefficient ($a^{-1}da/dT$) was virtually identical to that for the protonated species. We therefore discount solvation or viscosity effects as sources of the temperature dependence, and restrict discussion to modulation of the proton hfi by vibrational modes of the radical.

A simple harmonic oscillator modulates hfi's *via* even powers of the displacement coordinate,[25] since odd powers average to zero for a Hermitian function:

$$a(Q) = a_0 + a_2\langle Q^2\rangle + a_4\langle Q^4\rangle + \cdots , \tag{3}$$

where the use of averages is justified by the much greater values of the vibrational frequencies compared to the hyperfine frequency. Retaining the quadratic term only, and averaging over a Boltzmann population of the vibrational levels, the expected temperature dependence due to the entire collection of vibrational normal modes is of the form:[26]

$$a(T) = a_0 + \sum_i a_2^i \frac{h}{8\pi^2 \nu_i} \coth\left[\frac{h\nu_i}{2K_B T}\right] , \tag{4}$$

where K_B is the Boltzmann constant and

$$a_2^i=\frac{1}{2}\frac{\partial^2(a)}{\partial Q_i^2} \tag{5}$$

is half of the second derivative of the hfi with respect to the normal coordinate Q_i.

At sufficiently high temperatures expression (4) approximates to

$$a(T)=a_0+\sum_i a_2^i\frac{K_B}{4\pi^2\nu_i^2}T=a_0+\sum_i b_1^iT\ , \tag{6}$$

where $\sum_i b_1^i$ is independent of the mass of the isotope. This can be shown by recalling the reduced mass dependence of the normal coordinate, $Q_i=X_i\sqrt{\mu_i}$, and rearranging the expression for the slope as follows:

$$\sum_i b_1^i=\sum_i\frac{1}{2}\frac{\partial^2(a)}{\partial Q_i^2}\frac{K_B}{4\pi^2\nu_i^2}=\sum_i\frac{1}{2}\frac{\partial^2(a)}{\partial X_i^2}\frac{K_B}{F_i}\ , \tag{7}$$

where μ_i is the reduced mass and $F_i=4\pi^2\nu_i^2\mu_i$ is the force constant of the ith normal mode. We can hence rewrite Eq. (4) in terms of the b_1^i coefficients, as follows:

$$a(T)=a_0+\sum_i b_1^i\frac{h\nu_i}{2K_B}\coth\left[\frac{h\nu_i}{2K_BT}\right]\ . \tag{8}$$

Because of the contribution of high-frequency modes, a straight line with slope $\sum_i b_1^i$ is obtained only at extremely high temperatures, normally not accessible to experimental observation. In practice, over the experimentally accessible temperature range, the high-temperature limit applies only to low-frequency modes, while high-frequency modes contribute essentially a constant value (the ground vibrational contribution).

The simplest situation corresponds to a *one-mode* model, where only one low-frequency mode contributes to the temperature dependence and all the remaining modes either have frequencies that are too high, or negligible b_1^i coefficients. In this case Eq. (6) becomes

$$a(T)=a_0'+b_1^kT\ , \tag{9}$$

where k identifies the mode *active* in determining the temperature dependence, a_0' includes the constant contribution due to high-frequency modes, and b_1^k can be compared directly with the experimentally observed slope.

By assuming this model, we can estimate from our data in liquid toluene a frequency of $\sim 120\ \mathrm{cm}^{-1}$ for the mode responsible for the temperature effect. This was done by multiplying the observed slope by successive values of $h\nu/2K_B$ and regenerating $a(T)$ from (8) for various ν [Fig. 1(a)].

The value obtained is extremely low. Compared to the results of the force field calculation, it is one-half of the lowest computed vibrational frequency. Given the excellent agreement between QCFF-PI computed and observed vibrational frequencies for C_{60} and related compounds,[19–21] we believe that a similar degree of accuracy obtains the force field of HC_{60} discussed here. Therefore, we ascribe the discrepancy between the QCFF-PI computed frequencies and the estimate deduced above to the inadequacy of the *one-mode* model. Nevertheless, the approximate frequency deduced from this model indicates that modes dominated by hydrogen motion will play almost no role in determining the observed temperature dependence.

To check the above conclusion, we have computed the second derivatives $2a_2^i$ as described in the previous section and obtained an estimate of the b_1^i term for each vibrational normal mode. Notice that, because of the ν_i^2 term in Eq. (7), higher-frequency modes need much larger derivatives in order to contribute non-negligible b_1^i coefficients. Moreover, high-frequency modes will contribute essentially to a_0' while only low-frequency modes will contribute to the slope of the straight line observed experimentally.

The largest b_1^i parameters are listed in Table I. The calculation indicates that below 800 cm^{-1} only two modes show large b_1^i values. These are the lowest A'' frequency mode (calculated at 245 cm^{-1}) for which we obtain a very large (in absolute value) b_1 coefficient (-1.45 kHz/deg), and the A'' mode at 386 cm^{-1} for which we calculate a smaller but still considerable contribution ($b_1=-0.86$ kHz/deg). It is worth mentioning that these two modes correspond to the lowest h_g and h_u vibrational frequencies of C_{60}.[19] Two additional A'' vibrations, in the higher-frequency region, also show large negative contributions: a mode whose computed frequency is 1225 cm^{-1} ($b_1=-0.64$ kHz/deg) and an even higher-frequency mode, at 1322 cm^{-1}, for which the calculated b_1 coefficient is -1.04 kHz/deg.

The remaining A' and A'' modes show much smaller contributions, with the exception of the modes describing the hydrogen motions discussed in the previous section. The results presented in Table I show that the b_1^i coefficients of these modes are large and positive: 1.09 and 0.33 kHz/deg, for the two components of the CH wagging (1156 and 1168 cm^{-1}, respectively), 1.54 kHz for the CH rock and 0.95 kHz/deg for the CH stretch.

Because of their fairly high frequencies these modes in practice do not contribute to the observed temperature dependence but, as we will show in the following, their inclusion in a *multimode* model is of fundamental importance in explaining the proton-muon hyperfine anomaly.

In summary, calculations indicate that most of the normal modes of HC_{60} involving C_{60}-like motions contribute with negative b_1^i to Eq. (8). Only four of them show very large contributions. Large b_1^i values are also predicted for the modes describing the hydrogen motion and, contrary to most of the C_{60}-like modes, the sign of these contributions is positive.

The motion of the hydrogen atom in the CH wagging normal coordinate of HC_{60} can be compared to that of the hydrogen in torsional modes of simple alkyl radicals, since in both cases the hydrogen moves far away from the conformation in which it eclipses the unpaired electron localized on the p orbital of the α carbon. Because of this motion, the temperature dependence of the torsional mode in the latter radicals is negative,[27] a result which is opposite to the effect computed here for the CH wagging mode in HC_{60}. In fact, compared to alkyl radicals, where

TABLE I. Computed b_1^i parameters (kHz/deg) for HC_{60} vibrational normal modes.

A'			A''						
ν_i	b_1^i [a]		ν_i	b_1^i [a]		ν_i	b_1^i [a]	ν_i	b_1^i [a]
2993	0.95	CH stretch	1603	−0.30		1111	−0.16	621	−0.13
1429	0.13		1500	−0.22		1071	0.29	604	0.20
1294	1.54	CH rock	1411	−0.16		995	−0.18	599	−0.12
1216	0.19		1391	−0.23		984	0.25	582	−0.12
1187	0.10		1348	−0.30		967	0.14	526	−0.11
1110	0.12		1338	−0.10		827	0.24	519	−0.11
1069	0.17		1322	−1.04		826	0.26	464	−0.12
986	0.28		1246	−0.16		795	−0.13	431	−0.13
836	0.43		1228	−0.20		794	−0.13	395	−0.19
467	−0.11		1225	−0.64		718	−0.24	386	−0.86
250	−0.11		1168	0.33		712	−0.11	357	0.10
			1156	1.09	CH wag	686	0.13	255	−0.13
			1143	−0.16		682	−0.13	245	−1.45

[a] Only contributions larger than 0.1 kHz/deg are listed.

the unpaired electron is substantially localized on a single α carbon, the situation in HC_{60} is complicated by the well-established[6,4,7] delocalization of the unpaired spin over a number of carbon atoms close to the hydrogen. In particular, it has been shown that the β-proton hfi is determined by the sum of the contributions of the three α carbons.[6,4] Since displacements along normal coordinates will change the overall distribution of the unpaired spin, the collective effect of the three α carbons must be taken into account. In fact, we have verified that spin populations change in such a way that the sum of the α-carbon contributions, according to Whiffen's equation,[28] is larger at a geometry displaced along the CH wagging than at the equilibrium geometry, a result which explains the positive value of b_1. Similar considerations explain the hfi decrease when the molecule is displaced along the *active* C_{60}-like normal modes discussed above. These results demonstrate a fundamental difference between HC_{60} and alkyl radicals, and lend further support to the suggestion that the unpaired electron is not localized on a single carbon. It is this partial delocalization that causes the peculiar effect of CH wagging on the proton hfi in HC_{60} as compared to alkyl radicals.

It is interesting to note that, among the A' normal modes, only the CH rock and stretch have a large b_1 coefficient. Most of the remaining modes show very small contributions, which indicates that for the C_{60}-like normal modes the dominant contribution to Eq. (3) is the linear term $a_1^i \langle Q_i \rangle$ which averages to zero.

On the basis of the calculated b_1^i we can now simulate the temperature dependence using a *multimode* model involving all the normal modes of HC_{60}. In the simulation we assume that the total b_1 factor for "pure" CH wagging is the sum of the contributions of the two modes of frequency 1156 and 1168 cm^{-1}. By adjusting the a_0' coefficient to 92 700 kHz we obtain the fit shown by the dotted line in Fig. 1(b). It is seen that the agreement between the computed and observed temperature dependence is satisfactory. The simulation correctly predicts a negative temperature dependence, which is mainly due to the two A'' low-frequency modes (245 and 386 cm^{-1}) discussed above. However, the computed slope is slightly smaller than the observed. By scaling the b_1^i coefficients of the lowest-frequency modes (the only frequencies that can affect the temperature dependence in the observed range) by 1.2 and adjusting the a_0' parameter to 93 250 kHz we obtain the fit shown by the dashed line in the same figure. It indicates that a very small scaling factor is enough to reproduce almost exactly the observed temperature dependence.

A most striking effect is apparent in Fig. 2, where an expanded scale is used to show the temperature dependence of the "reduced" muon hfi ($a_{\mathrm{Mu}}\gamma_H/\gamma_{\mathrm{Mu}}$). Muoni-

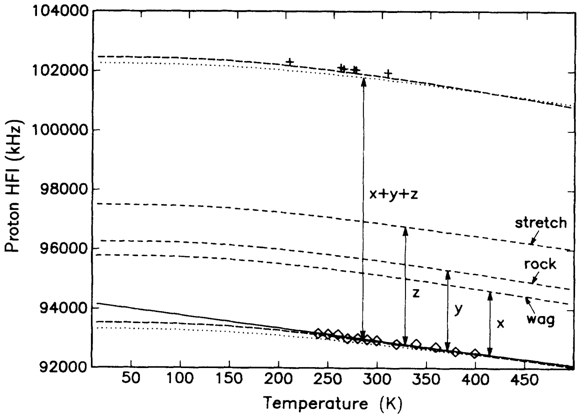

FIG. 2. Observed and computed proton-muon anomaly: (diamonds) HC_{60} experimental data in liquid toluene; (crosses) MuC_{60} experimental data from Refs. 11 and 12; (dotted line) "reduced" muon and proton hfi computed using the *multimode* model with b_1^i parameters computed for all the vibrational normal modes and $a_0' = 92\,700$ kHz; (long-dashed line) "reduced" muon and proton hfi computed using the *multimode* model with the b_1^i parameters of the 70 lowest-frequency modes scaled by 1.2 and $a_0' = 93\,250$ kHz (see discussion in the text); (short-dashed line) contributions of CH stretching, rocking, and wagging to the isotope effect.

um can be regarded as a light "isotope" of hydrogen:[29] its mass is approximately one-ninth that of the proton, its magnetic moment is 3.183 35 times larger, and it has an identical nuclear spin ($I=\frac{1}{2}$). At 210 K, the Mu hfi in MuC_{60} is 325.7 MHz,[4,12] compared to 93.35 MHz for HC_{60} in toluene at the same temperature. The ratio of these numbers is 3.49, representing a hyperfine anomaly of nearly 10%. Anomalies of this size or larger, and of the same sign, are common amongst alkyl radicals,[30,31] and have been attributed to differences in torsional averaging about C-C bonds.[32] The two sets of dotted and dashed lines depicted in Fig. 2 correspond to the simulation of the temperature dependence of the proton and "reduced" muon hfi using the model and parameters described above. Clearly, our calculations indicate that inclusion of the three modes describing the hydrogen motions, although almost ineffective as regards the temperature dependence, causes a strong increase of the "reduced" muon hfi that corresponds fairly closely to the observed proton-muon anomaly. Although other mechanisms, such as anharmonicity in the CH stretch,[33] can, in principle, be partially responsible for the H-Mu anomaly, the simulations presented in Fig. 2 strongly suggest that hfi modulation by the three molecular vibrations dominated by hydrogen motions is the most likely origin since it essentially accounts for the whole observed effect.

Finally we note that the three modes contribute roughly the same amount to the isotope effect, as shown by the three short-dashed lines also depicted in Fig. 2. The latter result is at variance with a very recent *ab initio* study[34] where it was found that the contributions from CCH bends is negligible. The difference between our result and that reported in Ref. 34 can be ascribed to two factors: first, the *ab initio* spin-density distribution obtained with minimal basis set[5] is much more localized on one of the three α carbons than the semiempirical results and EPR spectra indicate. Second, to obtain the hfi variations we displaced the radical along its vibrational normal coordinates which, particularly in the case of CCH bends, involve motions of atoms other than the hydrogen.

In conclusion, the present study based on quantum-chemical evaluation of the force field of HC_{60} accounts for both the temperature dependence and isotope effect of the hydrogen hyperfine coupling of HC_{60}.

We are indebted to Dr. Willem Siebrand of this Institute for helpful discussion and to R. Dutrisac for technical assistance. We would also like to thank Dr. E. Roduner and Dr. H. Fischer (ETH, Zurich) for suggesting the benzophenone-isopropanol method of generating H atoms in solution. This work was supported by the NRCC through Grant No. 37233.

---

[*] Permanent address: Dipartimento di Chimica "G. Ciamician," Università di Bologna, 40126 Bologna, Italy.

[1] P. J. Krusic *et al.*, Science **254**, 1183 (1991); J. R. Morton *et al.*, J. Chem. Soc. Perkin Trans. **2**, 1425 (1992); P. J. Krusic *et al.*, J. Phys. Chem. **97**, 1736 (1993); P. N. Keizer *et al.*, J. Chem. Soc. Perkin Trans. **2**, 1041 (1993).

[2] J. P. Hare and H. W. Kroto, Acc. Chem. Res. **25**, 106 (1992); H. W. Kroto and M. Jura, Astron. Astrophys. **263**, 275 (1992).

[3] J. R. Morton *et al.*, Chem. Phys. Lett. **204**, 481 (1993).

[4] P. W. Percival and S. Wlodek, Chem. Phys. Lett. **196**, 317 (1992).

[5] T. A. Claxton and S. F. J. Cox, Chem. Phys. Lett. **207**, 31 (1993).

[6] J. R. Morton, F. Negri, and K. F. Preston, Can. J. Chem. (to be published).

[7] N. Matsuzawa, D. A. Dixon, and P. J. Krusic, J. Phys. Chem. **96**, 8317 (1992).

[8] D. M. Chipman, J. Phys. Chem. **96**, 3294 (1992).

[9] I. D. Reid and E. Roduner, Hyperfine Interact. (to be published).

[10] B. Addison-Jones *et al.*, Hyperfine Interact. (to be published).

[11] E. J. Anseldo, C. Niedermayer, and C. E. Stronach, Nature **353**, 121 (1991); E. J. Anseldo *et al.*, Z. Phys. B **86**, 317 (1992).

[12] R. F. Kiefl *et al.*, Phys. Rev. Lett. **68**, 2708 (1992).

[13] D. Griller, Magn. Reson. Rev. **5**, 1 (1979).

[14] A. J. Colussi, J. R. Morton, and K. F. Preston, Chem. Phys. Lett. **30**, 317 (1975).

[15] J. K. S. Wan and A. J. Elliot, Acc. Chem. Res. **10**, 161 (1977).

[16] F. J. Adrian, Rev. Chem. Intermed. **3**, 3 (1979).

[17] F. Zerbetto *et al.*, J. Chem. Phys. **89**, 3681 (1988); F. Negri *et al.*, *ibid.* **90**, 5944 (1989).

[18] A. Warshel and M. Karplus, J. Am. Chem. Soc. **94**, 5612 (1972); A. Warshel and M. Levitt, Quantum Chemistry Program Exchange No. 247, Indiana University, 1974.

[19] F. Negri, G. Orlandi, and F. Zerbetto, Chem. Phys. Lett. **144**, 31 (1988); **190**, 174 (1992).

[20] F. Negri, G. Orlandi, and F. Zerbetto, J. Am. Chem. Soc. **113**, 6037 (1991).

[21] F. Negri, G. Orlandi, and F. Zerbetto, Chem. Phys. Lett. **196**, 303 (1992).

[22] F. Dushinsky, Acta Phisicochim. USSR **7**, 551 (1937).

[23] M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc. **99**, 4899 (1977); **99**, 4907 (1977); M. J. S. Dewar, M. L. McKee, and H. S. Rzepa, *ibid.* **100**, 3607 (1978); M. J. S. Dewar and J. J. P. Stewart, Quantum Chemistry Program Exchange No. 506, Indiana University, 1986.

[24] M. J. S. Dewar, J. A. Hashmall, and C. J. Venier, J. Am. Chem. Soc. **90**, 1953 (1968).

[25] D. M. Schrader, J. Chem. Phys. **46**, 3895 (1967); R. W. Fessenden, *ibid.* **71**, 74 (1967).

[26] R. E. Moss, Mol. Phys. **10**, 339 (1966).

[27] J. C. Scaiano and K. U. Ingold, J. Phys. Chem. **80**, 275 (1976).

[28] D. H. Whiffen, Mol. Phys. **6**, 223 (1963).

[29] E. Roduner and H. Fischer, Chem. Phys. **54**, 261 (1981).

[30] E. Roduner *et al.*, Chem. Phys. Lett. **57**, 37 (1978).

[31] E. Roduner *et al.*, Chem. Phys. **67**, 275 (1982).

[32] P. W. Percival *et al.*, Chem. Phys. Lett. **133**, 465 (1987).

[33] P. W. Percival *et al.*, Chem. Phys. Lett. **163**, 241 (1989).

[34] M. A. Boxwell, T. Claxton, and S. T. Cox, J. Chem. Soc. Faraday Trans. **89**, 2957 (1993).