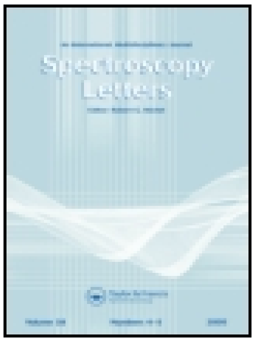

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J. F. Ogilvie

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THE PLANARITY OF THE METHYL RADICAL

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by J.F. Ogilvie

Department of Chemistry, Memorial University of Newfoundland,
St. John's, Newfoundland, Canada A1C 5S7

Abstract: The evidence of the photo-electron spectrum is reanalysed to indicate that the methyl radical is probably planar in its ground state, but must be at least quasi-planar.

The question of the planarity of the equilibrium conformation of the methyl radical CH_3 is of considerable current interest. Koenig, Balle and Snell[1] concluded that their photo-electron spectrum indicated non-planarity of the radical in its ground state. Blustin and Linnett[2] were confident that their molecular orbital computations indicated CH_3 to be appreciably non-planar in the ground state. These recent conclusions are generally contrary to previous deductions from both experiment and quantum calculations, although some workers have been careful to state that a small deviation from planarity could not be excluded. Linnett and Poë[3] estimated a deviation from planarity of 11 - 19°, and Walsh[4] estimated that the radical was non-planar but had a smaller barrier to inversion than ammonia. The valence-bond semi-empirical method led Jordan and Longuet-Higgins[5] to predict that the planar CH_3

radical would resist quite strongly out-of-plane deformation. Herzberg[6] concluded that the deviation from planarity compatible with the electronic spectrum must be less than 10°. Both Herzberg's C-D bondlength[6] of 1.079×10^{-10}m and average bond-dissociation energy[7] of $\lesssim 6.8\times10^{-19}$J are consistent with a planar or nearly planar molecule, according to Bernstein's correlations[8] and observed and estimated wavenumbers of C-H stretching fundamentals.[9] However, the appearance in the electronic spectrum of a vibrational interval attributed to an overtone of the out-of-plane deformation mode in the ground state[6] suggests, because the transition was from the ground to an excited Rydberg (ion-like) state, that a change of conformation may occur between the two states - i.e., both states might not be planar. Also the gas-phase absorption spectrum of the methyl radical[10] showed multiple band centres which were explained, perhaps not conclusively, as including hot-band transitions. Thus the planarity of the methyl radical seems open to question.

The wavenumber of the mode describable as out-of-plane deformation (in the limiting case of planarity, D_{3h} point group) is fairly well established[9,10,11] to be in the range 60.2 - 61.7 mm^{-1}, probably at 60.70 mm^{-1} in the gas phase[10], for the species $^{12}C^{1}H_3$. If both planar equilibrium conformation and a purely harmonic potential function for the out-of-plane deformation co-ordinate θ (in radians) are assumed, then the potential function for this mode is separable by reason of its unique A_2''

symmetry class, of the form

$$2\,V = k\,\theta^2$$

where θ is the angular deviation from planarity. The harmonic force constant k can be calculated from the relation[12]

$$k = 4\pi^2 c^2 \nu^2 R^2_{C-H}\,/(3/m_H + 9/m_C)$$

to be $6.782\text{x}10^{-20}$ J rad^{-2}. This magnitude is relatively small; it may be compared with $4.48\text{x}10^{-19}$ J rad^{-2} for $^{10}B^{19}F_3$, which is more representative of known molecules of the D_{3h} point group. Possibly more revealing are the amplitudes of this ν_2 vibration in the zero-point energy state, calculated from the relation

$$2\,\theta_t = \cdot\,(h(3/m_H + 9/m_C)/c\nu)^{\frac{1}{2}}/\pi R_{C-H}$$

for the classical turning points $\pm\,\theta_t$. The amplitudes are 48.3° for CH_3, 43° for CD_3, but 19.7° for BF_3. Thus at these turning points, the angular deviations from planarity are 24.1° for CH_3, 21.5° for CD_3, and 9.8° for BF_3, corresponding to interbond (H-C-H etc.) angles of 104.4°, 107.4° and 117.1° rad respectively, compared with 120° in the planar molecules. The deviations from planarity deduced by Koenig et al[1], about 5° and by Blustin and Linnett[2], (less than) 18°, are both smaller than the computed half-amplitude of 24.1° for CH_3. Although the harmonic approximation is not accurate, the conclusion that deviation from planarity of equilibrium conformation must be less than, or comparable to, this calculated zero-point vibrational amplitude is at least qualitatively valid. In fact a similar magnitude of half-amplitude of vibration is obtained when the anharmonic potential function of

Riveros[13] is used, although this potential was based on wavenumbers of the matrix-isolated, not free, molecule. Thus the methyl radical seems to be at least quasi-planar.

Under the assumption that the interval of 72.0 mm^{-1} in the vibrational progressions of the photo-electron spectrum detected by Koenig et al[1] is real (previously published spectra[14] did not show these features), the interpretation is rather more complex than was suggested by Koenig et al[1]. There are at least four possible cases.

(i) This interval represents ν_2' of the planar CH_3^+ cation, the radical ground state is also planar, and the appearance of this non-totally symmetric fundamental (A_2'' of D_{3h}) is vibronically induced because of a marked variation of the electronic wavefunction over the large zero-point amplitude. But if both states are planar, there is no obvious hybridisation change, so this explanation seems unlikely. Orbital following, if operative, could perhaps facilitate this mechanism.

(ii) The interval represents ν_2' of a non-planar CH_3^+ cation, and thus ν_2' is totally symmetric (A_1 of C_{3v}) and hence allowed. The appearance of this vibrational mode in the electronic transition could indicate a change of angle between the two states. Also a substantial barrier to planarity would be required in CH_3^+ such that the inversion splitting was small, because only the $(1^+)' \leftarrow (0^-)''$ transition would be allowed without vibronic interaction. The calculated zero-point amplitude effectively eliminates this possibility. Furthermore, as there is no evidence to suggest that the methyl cation is non-planar, this explanation seems even more unlikely.

(iii) The interval is $2\nu_2'$, allowed because of a large change in wavenumber during the ionisation transition. This explanation would be consistent with the relative magnitudes of ν_2'' and ν_2', 60.7 and 36.0 mm^{-1} respectively, and would mean that both states were planar. A lack of marked anharmonicity is also implied; the ground state is believed to have a very anharmonic potential function for this out-of-plane deformation mode[10,13], although this mode in the ionic state seems to be nearly harmonic[1]. This mechanism may possibly explain the observation of the overtone in the electronic spectrum[6].

(iv) The interval is $2\nu_2'$, and the vibrational progressions are observable according to the Franck-Condon principle because the ground state is non-planar or quasi-planar.

The fourth case seems to be that concluded by Koenig _at al_[1], but they erroneously attributed the vibrational interval to ν_2' instead of $2\nu_2'$. The marked change of ν_2 between the two electronic states can also be characteristic of transition with significant structural changes, such as angular to linear conformations to triatomic molecules[15]; however a large structural change seems not possible for the methyl radical in a transition from a quasi-planar (at most) ground state to a planar excited state. The harmonic force constant for the ground state of the cation for the out-of-

-plane deformation mode is $(2.6 \pm 0.8) \times 10^{-20}$ J rad^{-2}; a C-H bondlength of 1.124×10^{-10} m, as found[6] in the Rydberg state $^2A'$ at 4662.85 mm^{-1}, is assumed. Thus the evidence from the photo-electron spectrum[1] for non-planarity is at best inconclusive.

In the $A^1A_2'' \leftarrow X^1A$ transition of NH_3, from a definitely non-planar ground state to a Rydberg state of established planarity[15], the wavenumber of ν_2 changes only slightly, from 95.0 to 87.8 mm^{-1}. However in this Rydberg state there still remains one electron in the $2p_\pi$-orbital of nitrogen; the presence of these p_π-non-bonding electrons in triatomic molecules is known to be associated with increased wavenumber of deformation modes[16]. Thus the applicability of this precedent to the methyl radical seems doubtful.

If the correct interpretation of the methyl photo-electron spectrum is case (iv) meaning a non-planar ground state, there are implications for both the out-of-plane potential function of the radical and the electron paramagnetic resonance spectrum. The simplest appropriate potential function for this deformation mode (no longer strictly separable from the symmetric C-H stretching motion, also of class A_1 of point group C_{3v}, in the harmonic limit) would be

$$V = k_2\theta^2/2 + k_4\theta^4/24 ,$$

with $k_2 < 0$ and $k_4 > 0$. Thus the sign of k_2 must be different from that employed by Riveros[13], and Pimentel et al[10] in their attempts to fit the observed vibrational wavenumbers to a simple potential. These coefficients can be related by the expression

$$k_2 = -k_4 \theta_e^2/6$$

in which θ_e is the angle of deviation from planarity in the equilibrium conformation. (For comparison, a purely harmonic potential function, i.e. $k_2 > 0$ and $k_4 = 0$, enables an accurate prediction of ν_2 of $^{11}B^{19}F_3$ from k_2 derived for $^{10}B^{19}F_3$). If the equilibrium conformation is non-planar, then there can be a direct Fermi contact contribution to the proton hyperfine-splitting constant at the equilibrium conformation, as well as at less probable conformations assumed during zero-point vibrational motion. This effect, as well as hyperconjugation (or configuration interaction with excited states), will give positive contributions to the coupling constant a_H, whereas spin polaristation, the dominant effect, leads to an overall negative coupling constant. The temperature dependence of the coupling constant could provide useful information[17] about the structure, provided that there were no radical-solvent interactions with a measurable temperature dependence to complicate the interpretation.

In summary, the evidence of the photo-electron spectrum[1] by no means unambiguously indicates that the methyl radical has a non-planar ground state (case iv). In fact the evidence seems to favour a planar ground state of both radical and cation (case iii), although the resistance to out-of-plane deformation is relatively small in both states. In either case, the wavenumber of the ν_2 mode of the cation seems to be 36.0 mm^{-1}, not 72.0 mm^{-1} as earlier suggested[1]. An insufficiently large basis set may be one reason for the misleading result of the molecular orbital calculations of Blustin and Linnett[2].

By analogous calculation, one can show that the methylene radical[18,19] probably becomes quasi-linear only when $v_2 \gtrsim 2$.

REFERENCES

1. T. Koenig, T. Balle and J.W. Snell, J. Amer. Chem. Soc., 97, 662 (1975).
2. P.H. Blustin and J.W. Linnett, J. Chem. Soc. Faraday II, 71, 1058 (1975).
3. J.W. Linnett and A.J. Poë, Trans. Faraday Soc., 47, 1033 (1951).
4. A.D. Walsh, J. Chem. Soc. (London), 2296 (1953).
5. P.C.H. Jordan and H.C. Longuet-Higgins, Mol. Phys., 5, 121 (1962).
6. G. Herzberg, Proc. Roy. Soc. (London), A262, 291 (1961).
7. G. Herzberg, Can. J. Phys., 39, 1511 (1961).
8. H.J. Bernstein, Spectrochim. Acta, 18, 161 (1962).
9. A. Snelson, J. Am. Chem. Soc., 74, 537 (1970).
10. L.Y. Tan, A.M. Winer and G.C. Pimentel, J. Chem. Phys., 57, 4028 (1972).
11. D.E. Milligan and M.E. Jacox, J. Chem. Phys., 47, 5146 (1967).
12. L.H. Jones, Inorganic Vibrational Spectroscopy, Dekker, New York, 1971, page 191.
13. J.M. Riveros, J. Chem. Phys., 51, 1269 (1969).

14.a) L. Golob, N. Jonathan, A. Morris, M. Okuda and K.J. Ross, J. Electron Spectrosc. Relat. Phenonena, 1, 506 (1973).
   b) A.W. Potts, K.G. Glenn and W.C. Price, Faraday Disc. 54, 65 (1972).

15. A.W. Potts and W.C. Price, Proc. Roy. Soc. (London), A326, 181 (1972).
16. G. Herzberg, Adv. Photochem., 5, 1 (1968).
17. J.M. Riveros, An. Acad. Brasil. Cienc., 42, 181 (1970).
18. G. Herzberg and J.W.C. Johns, J. Chem. Phys., 54, 2276 (1971).
19. J.F. Ogilvie, Can. J. Chem., 46, 2472 (1968).

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