Raman Spectrum of the Potassium Salt of Chloranil (2,3,5,6-Tetrachloro-*p*-benzoquinone) Radical Anion

By Alberto Girlando, Renato Bozio, and Cesare Pecile*
(*Institute of Physical Chemistry, The University, via Loredan* 2, 35100 *Padua, Italy*)

Summary The Raman spectrum of chloranil monovalent radical anion has been obtained; it is strikingly different from that of the parent compound, and some preliminary assignments are discussed.

There have been relatively few reports on the vibrational behaviour of strong electron acceptor or donor molecules (EDA) and of their radical ions, and these are limited to interpretations of i.r. data.[1–4] The advent of laser Raman spectroscopy and a more extended use of single-crystal studies has led to a systematic investigation of some representative EDA molecules: tetracyanoethylene (TCNE),[5] 7,7,8,8-tetracyanoquinodimethane (TCNQ),[6] and chloranil (CA).[7] Such a systematic approach allows the possibility of a rationalization, until now undertaken for i.r. spectra only, of the vibrational behaviour of the corresponding radical anions,[2–4] but Raman data are necessary for this, particularly for the above structures which belong to the D_{2h} point group. With the exception of *p*-phenylenediamine radical cation,[8] no Raman spectra of EDA radical ions have appeared, as far as we know.

We report here the Raman spectrum of $K^+CA^{\overline{\cdot}}$ powder obtained using the rotating cell technique.[9] The salt was prepared according to the method of Torrey and Hunter[10] and sprinkled into the sampling cavity on a base layer of KBr and pressed at *ca.* 20 bar. The occurrence of rapid decomposition in static sampling necessitated the use of the rotating cell technique. A careful check by Raman and i.r spectroscopy showed that this difficulty was completely overcome with the rotating cell.

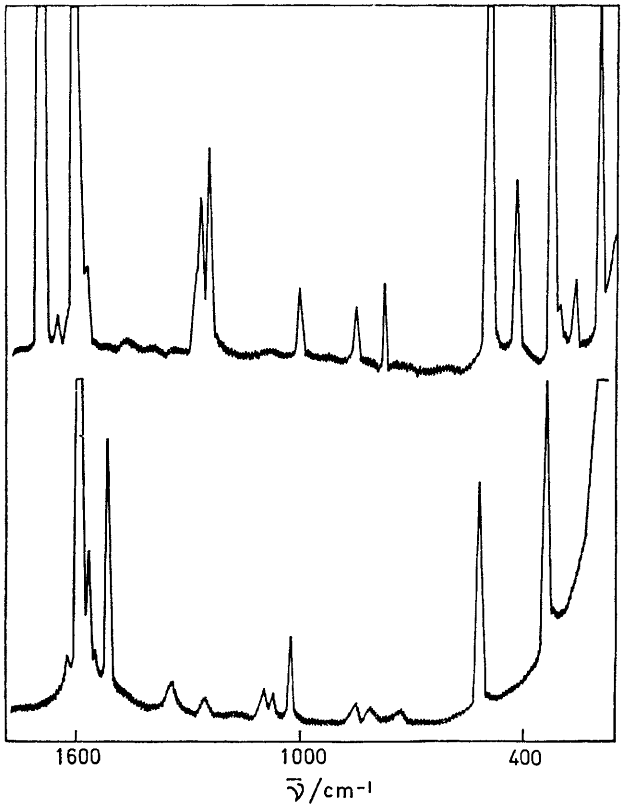

FIGURE. Raman spectra of powdered CA (upper part) and K$^+$CA$^{\overline{\cdot}}$ (lower part). Exciting line: 514·5 nm.

The spectrum of K$^+$CA$^{\overline{\cdot}}$ recorded on a Jarrel-Ash 25-300 spectrometer with 514·5 nm excitation from a Spectra Physics Argon ion laser (mod. 165) is shown in the Figure (lower part) in the range 150—1800 cm^{-1}. The exciting frequency is sufficiently far from the centre of the K$^+$CA$^{\overline{\cdot}}$ electronic absorption bands[11] for the spectrum reported here not to be a resonance Raman one. The corresponding spectrum of neutral CA is in the upper part of the Figure.

Comparison between the Raman and i.r.[3,4] spectra of K$^+$CA$^{\overline{\cdot}}$ shows the absence of relevant vibronic effects (electron vibration) of the type invoked to explain the i.r. spectrum of TCNE$^{\overline{\cdot}}$.[2] There are clear differences between the Raman spectra of free CA[7] and that of its radical anion (Figure), as occurs in the i.r. region.[3,4] The five prominent lines of K$^+$CA$^{\overline{\cdot}}$ (Figure) can be associated with totally symmetric modes, in view both of their intensity and of an unambiguous correlation with the neutral molecule.[7] Their frequencies fit satisfactorily those calculated for the a_g modes by the same valence force field previously developed to reproduce the i.r.-active fundamentals: (calculated values in parentheses) 1592 (1545), 1514 (1503), 1026 (1034), 517 (485), and 336 (338) cm^{-1}. The corresponding frequencies of neutral CA are:[7] 1693 (1683), 1609 (1597), 1007 (1004), 496 (485), and 330 (332) cm^{-1}.

An approximate description in terms of the potential energy distribution of the a_g lines at 1592 and at 1514 cm^{-1} indicates that they correspond to practically pure C=C stretch and C=O stretch, respectively (located at 1609 and 1693 cm^{-1} in the neutral molecule). In the i.r.[4] an analogous situation is found for the b_{1u} C=O stretch at 1524 cm^{-1} and the b_{2u} C=C stretch at 1540 cm^{-1}, the former located at 1685 cm^{-1} and the latter at 1572 cm^{-1} in the neutral molecule. For the four fundamentals above, the frequency shift resulting from ionization of the neutral molecule is comparable for the corresponding i.r.- and Raman-active modes, and is predictable in terms of the variations of the diagonal force constants only. Therefore, these vibrational modes reflect the rearrangements of bond orders[12] consequent upon the acceptance of an extra electron into the antibonding orbital of the *p*-quinone skeleton. However, the interpretation of the i.r. spectrum previously reported[4] shows that the variation of some off-diagonal force constants is necessary to account for the other spectral changes.

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[1] H. Kainer and W. Otting, *Chem. Ber.*, 1955, **88**, 1921; Y. Matsunaga, *J. Chem. Phys.*, 1964, **41**, 1609.
[2] J. C. Moore, D. Smith, Y. Youhne, and J. P. Devlin, *J. Phys. Chem.*, 1971, **75**, 325; Y. Iida, *Bull. Chem. Soc. Japan*, 1973, **46**, 423.
[3] Y. Iida, *Bull. Chem. Soc. Japan*, 1970, **43**, 345.
[4] A. Girlando, L. Morelli, and C. Pecile, *Chem. Phys. Letters*, 1973, **22**, 553.
[5] B. Moszynska, *Acta Phys. Pol.*, 1968, **33**, 959, and references therein.
[6] A. Girlando and C. Pecile, *Spectrochim. Acta*, 1973, **29*A***, 1859.
[7] A. Girlando and C. Pecile, *J.C.S. Faraday II*, 1973, **69**, 1291.
[8] E. Mayer, R. B. Girling, and R. E. Hester, *J.C.S. Chem. Comm.*, 1973, 192.
[9] W. Kiefer and H. J. Bernstein, *Appl. Spectr.*, 1971, **25**, 609; H. J. Sloane and R. B. Cook, *ibid.*, 1972, **26**, 589.
[10] H. A. Torrey and W. H. Hunter, *J. Amer. Chem. Soc.*, 1912, **34**, 702.
[11] N. Sakai, I. Shirotani, and S. Minomura, *Bull. Chem. Soc. Japan*, 1971, **44**, 675.
[12] G. Giacometti, P. L. Nordio, and G. Rigatti, *Nuovo Cimento*, 1962, **23**,433.