

Advances in Infrared and Raman Spectroscopy

VOLUME 10

Edited by
R.J.H. Clark and R.E. Hester

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Edited by

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A Wiley Heyden Publication



JOHN WILEY & SONS

Chichester · New York · Brisbane · Toronto · Singapore

8550193

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British Library Cataloguing in Publication Data:

Advances in infrared Raman spectroscopy.—Vol. 10

1. Infra-red spectrometry—Periodicals

2. Raman spectroscopy—Periodicals

535.84205 QC457

ISBN 0 471 26216 1

Photoset in Malta by Interprint Limited
and printed by Pitman Press, Bath

2210008

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FOREWORD TO THE SERIES

There are few areas of science which have not already benefited from the application of infrared spectroscopic methods, and progress in this field remains vigorous. Closely related information on chemical and biological materials and systems is obtainable from Raman spectroscopy, though there are also many important differences between the types of information yielded and the types of materials and systems best suited to study by each technique. The close relationship between these two sets of spectroscopic techniques is explicitly recognized in this Series. *Advances in Infrared and Raman Spectroscopy* contains critical review articles, both fundamental and applied, mainly within the title areas; however, we extend the coverage into closely related areas by giving some space to such topics as neutron inelastic scattering or vibronic fluorescence spectroscopy. Thus the Series is firmly technique orientated. Inasmuch as these techniques have such wide ranging applicability throughout science and engineering, however, the coverage in terms of topics will be wide. This integration of theory and practice, and the bringing together of different areas of academic and industrial science and technology, constitute major objectives of the Series.

The reviews are in those subjects in which most progress is deemed to have been made in recent years, or is expected to be made in the near future. The Series will appeal to research scientists and technologists as well as to graduate students and teachers of advanced courses. The Series is intended to be of wide general interest both within and beyond the fields of chemistry, physics and biology.

The problem of nomenclature in a truly international Series has to be acknowledged. We have adopted a compromise solution of permitting the use of either English or American spelling (depending on the origin of the review article) and have recommended the use of SI Units. A table of the international system of units is given on p. xiii for reference purposes.

R. J. H. CLARK
R. E. HESTER

PREFACE

The present volume begins with a detailed and polished account of the Raman spectroscopy of molecules in matrices. This review emphasises the importance of vibrational spectroscopy for the detection, identification and characterisation of trapped species. While accepting that, to this end, infrared spectroscopy has been more successful than Raman spectroscopy, the authors draw attention to the various successes achieved in Raman matrix experiments and discuss some of the practical problems which arise. Extensive tabular material is included. This review is followed by a shorter and more specific one dealing with the vibrational spectroscopy of the ammonium ion in crystals. Recent work on ammonium salts has tended to rely upon three techniques—vibrational spectroscopy, proton magnetic resonance spectroscopy and neutron scattering. All three areas are discussed, with emphasis on the first, with reference to topics such as hydrogen bonding, the role of the ammonium ion in phase transitions and the barrier heights to reorientation.

The third chapter recognizes the need we all have, if in any way involved in the use of lasers, to operate them safely and within the framework of national and international codes of conduct. This chapter, by a recognized ophthalmologist involved in the drawing up of such codes, acquaints the practitioner with the various hazards associated with laser radiation of different wavelengths, and then sets out clearly the appropriate laser classifications, safety standards, exposure limits, etc. This surely is essential reading for all operators of lasers, however skilful.

The volume then returns to more traditional lines with an authoritative review on the infrared and Raman spectra of molecular crystals. The review treats the lattice dynamics of molecular crystals and the calculation of crystal properties using model potentials in the harmonic and anharmonic approximations. This is followed by a review of the recent commercial instrumental developments in Fourier transform infrared spectrometry. Few areas of spectroscopy have seen such rapid, far-reaching and recent, developments on the instrumental front as has that discussed in this chapter. The review is timely and most informative in the evaluation it provides of the performance characteristics of the new model interferometers. The volume ends with an excellent, detailed account of the recent advances in vibrational photochemistry.

Following an introductory section dealing with unimolecular reactions induced by vibrational excitation, the review treats in depth reactions induced by both single photon and multiphoton vibrational excitation.

As with earlier volumes, we have favoured IUPAC nomenclature and the use of SI units. A table of SI units, and conversion factors from the units of other systems to SI units, is included on pp. xiii–xv.

October 1982

R. J. H. CLARK
R. E. HESTER

THE INTERNATIONAL SYSTEM OF UNITS (SI)

<i>Physical quantity</i>	<i>Name of unit</i>	<i>Symbol for unit</i>
--------------------------	---------------------	------------------------

SI Base Units

length	metre	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
temperature	kelvin	K
amount of substance	mole	mol

SI Supplementary Units

plane angle	radian	rad
solid angle	steradian	sr

SI Derived Units having Special Names and Symbols

energy	joule	$J = m^2 kg s^{-2}$
force	newton	$N = m kg s^{-2} = J m^{-1}$
pressure	pascal	$Pa = m^{-1} kg s^{-2} = N m^{-2} = J m^{-3}$
power	watt	$W = m^2 kg s^{-3} = J s^{-1}$
electric charge	coulomb	$C = s A$
electric potential difference	volt	$V = m^2 kg s^{-3} A^{-1} = J A^{-1} s^{-1}$
electric resistance	ohm	$\Omega = m^2 kg s^{-3} A^{-2} = V A^{-1}$
electric conductance	siemens	$S = m^{-2} kg^{-1} s^3 A^2 = \Omega^{-1}$
electric capacitance	farad	$F = m^{-2} kg^{-1} s^4 A^2 = C V^{-1}$
magnetic flux	weber	$Wb = m^2 kg s^{-2} A^{-1} = V s$
inductance	henry	$H = m^2 kg s^{-2} A^{-2} = V s A^{-1}$
magnetic flux density	tesla	$T = kg s^{-2} A^{-1} = V s m^{-2}$
frequency	hertz	$Hz = s^{-1}$
activity (radioactive)	becquerel	$Bq = s^{-1}$
absorbed dose (radiation)	gray	$Gy = J kg^{-1}$

SOME NON-SI UNITS

<i>Physical quantity</i>	<i>Name of unit</i>	<i>Symbol and definition</i>
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Decimal Multiples of SI Units, Some having Special Names and Symbols

length	ångström	$\text{\AA} = 10^{-10} \text{ m} = 0.1 \text{ nm}$ $= 100 \text{ pm}$
length	micron	$\mu\text{m} = 10^{-6} \text{ m}$
area	are	$a = 100 \text{ m}^2$
area	barn	$b = 10^{-28} \text{ m}^2$
volume	litre	$l = 10^{-3} \text{ m}^3 = \text{dm}^3$ $= 10^3 \text{ cm}^3$
energy	erg	$\text{erg} = 10^{-7} \text{ J}$
force	dyne	$\text{dyn} = 10^{-5} \text{ N}$
force constant	dyne per centimetre	$\text{dyn cm}^{-1} = 10^{-3} \text{ N m}^{-1}$
force constant	millidyne per ångström	$\text{mdyn \AA}^{-1} = 10^2 \text{ N m}^{-1}$
force constant	attojoule per ångström squared	$\text{aJ \AA}^{-2} = 10^2 \text{ N m}^{-1}$
pressure	bar	$\text{bar} = 10^5 \text{ Pa}$
concentration	—	$M = 10^3 \text{ mol m}^{-3}$ $= \text{mol dm}^{-3}$

Units Defined Exactly in Terms of SI Units

length	inch	$\text{in} = 0.0254 \text{ m}$
mass	pound	$\text{lb} = 0.453\,592\,27 \text{ kg}$
force	kilogram-force	$\text{kgf} = 9.806\,65 \text{ N}$
pressure	standard atmosphere	$\text{atm} = 101\,325 \text{ Pa}$
pressure	torr	$\text{Torr} = 1 \text{ mmHg}$ $= (101\,325/760) \text{ Pa}$
energy	kilowatt hour	$\text{kW h} = 3.6 \times 10^6 \text{ J}$
energy	thermochemical calorie	$\text{cal}_{\text{th}} = 4.184 \text{ J}$
thermodynamic temperature	degree Celsius ^a	$^{\circ}\text{C} \equiv \text{K}$

^a Celsius or 'Centigrade' temperature θ_{C} is defined in terms of the thermodynamic temperature T by the relation $\theta_{\text{C}}/^{\circ}\text{C} = T/\text{K} - 273.15$.

OTHER RELATIONS

1. The physical quantity, the wavenumber (units cm^{-1}), is related to frequency as follows:

$$\text{cm}^{-1} \approx (2.998 \times 10^{10})^{-1} \text{ s}^{-1}$$

2. The physical quantity, the molar decadic absorption coefficient (symbol ϵ) has the SI units $\text{m}^2 \text{ mol}^{-1}$. The relation between the usual non-SI and SI units is as follows:

$$\text{M}^{-1} \text{ cm}^{-1} = 1 \text{ mol}^{-1} \text{ cm}^{-1} = 10^{-1} \text{ m}^2 \text{ mol}^{-1}$$

3. It appears that for many years to come a knowledge of the 'electromagnetic CGS' unit system will be a necessity for workers in various fields of spectroscopy, but for practical purposes it is usually sufficient to note that for magnetic flux density, 1 gauss (G) corresponds to 10^{-4} T and for electric dipole moment, 1 debye (D) corresponds to approximately 3.3356×10^{-30} C m.

The SI Prefixes

<i>Fraction</i>	<i>Prefix</i>	<i>Symbol</i>	<i>Multiple</i>	<i>Prefix</i>	<i>Symbol</i>
10^{-1}	deci	d	10^1	deca	da
10^{-2}	centi	c	10^2	hecto	h
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{-18}	atto	a	10^{18}	exa	E

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Chapter 1

RAMAN STUDIES OF MOLECULES IN MATRICES

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'And ere a man hath power to say, "Behold!"
The jaws of darkness do devour it up:
So quick bright things come to confusion.'

INTRODUCTION

One of the most striking developments in recent chemical research has been the growing concern with the *mechanism* rather than the mere outcome of chemical reactions. This concern finds expression not only in the range and scope of modern kinetic studies and in the search for reaction intermediates but also in theoretical treatments at varying levels of sophistication. Perhaps the most direct way of determining how a reaction takes place is to identify and characterize the intermediate or intermediates through which it evolves. Such intermediates may be atoms, neutral molecules or ions; they may be in their electronic ground or excited states; and their lifetimes under normal conditions may vary from 10 to 10^{-12} s. One way of detecting these transient species involves chemical trapping, an approach which has been successful for example in elucidating the effect of electronic structure on the type and mechanism of reaction of the methylene diradical.⁽¹⁾ More direct, however, are methods involving the spectroscopic detection of the intermediate.

According to their lifetimes under normal conditions, short-lived species may be detected in mobile phases by either time-resolved or steady-state

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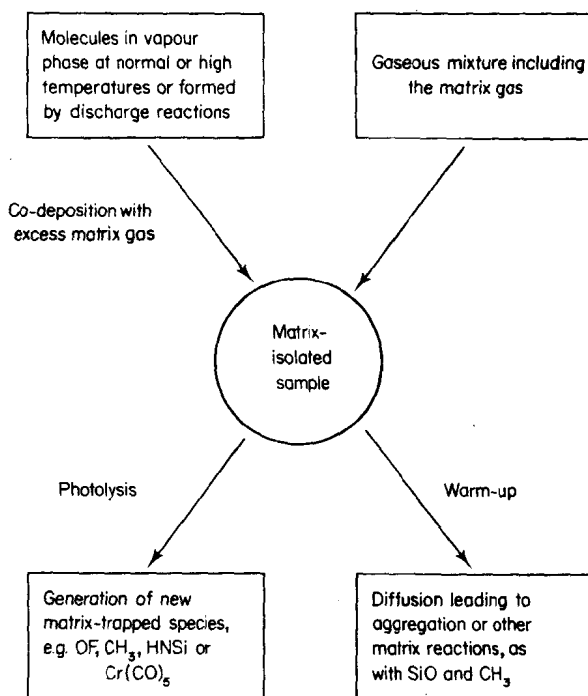
experiments. Thus, time-resolved measurements of optical spectra have proved a powerful device for monitoring the formation and decay of transient species like $\text{Cr}(\text{CO})_5$ ⁽²⁾ or OH ⁽³⁾ formed by flash-photolysis, pulse-radiolysis or shock-tube experiments with fluid samples. Durana and Mantz have exploited the increased sensitivity of the modern Fourier-transform infrared spectrometer to secure time-resolved infrared spectra of the HCO radical formed by flash photolysis of a mixture of CH_3CHO , He and CO .⁽⁴⁾ Alternative approaches to time-resolved infrared spectroscopy include the use of modulated electronic excitation with infrared detection (whereby the 2-hydroxyphenoxy radical has been detected for example)⁽⁵⁾ or of so-called 'time-resolved infrared spectral photography'.⁽⁶⁾ The second of these follows the absorption of a pulsed infrared continuum by 'upconversion' to the visible region by a four-wave mixing process; the visible light is then dispersed and photographed. Hence it is possible to observe the formation of the $(\text{CH}_3)_3\text{C}^\cdot$ radical by photolysis of $(\text{CH}_3)_3\text{CNO}$. The feasibility of recording resonance Raman spectra in the time-resolved mode has also been demonstrated, as witness the detection of $[\text{SCN}]_2^-$ ($t_1=1.6\ \mu\text{s}$) following pulse radiolysis of aqueous solutions of thiocyanate.⁽⁷⁾ Yet another means of detection is offered by the non-equilibrium distribution among electron spin states of a transient free radical generated by flash photolysis or pulse radiolysis; this may cause its e.s.r. signal to appear in emission (CIDEP).⁽⁸⁾ On the other hand, intermediates with lifetimes longer than about $10^{-4}\ \text{s}$ may lend themselves to examination by steady-state rather than relaxation experiments. In addition to the established methods of detection using ultraviolet-visible, microwave or e.s.r. spectroscopy, several new techniques have been successfully applied to the detection and characterization of species whose concentration has reached a steady state. Hence laser magnetic resonance⁽⁹⁾ gives access to transitions between Zeeman-split rotational sub-levels or between vibrational levels of molecules, as exemplified by its use in locating the bending fundamental of the gaseous CH_2 molecule.⁽¹⁰⁾ The enormous improvement in sensitivity and line-width made possible with the advent of the infrared diode laser has also been turned to spectacular advantage to record infrared spectra over a narrow frequency range at extremely high resolution; this approach has been applied, for example, to steady-state concentrations of simple gaseous molecules like ClO ,⁽¹¹⁾ CS ,⁽¹²⁾ NS ,⁽¹³⁾ SiO ,⁽¹⁴⁾ NF_2 ⁽¹⁵⁾ and CH_3 .⁽¹⁶⁾

Despite these recent improvements, however, there is an understandable appeal in alternative methods which extend the lifetime of the transient species and thereby allow direct spectroscopic examination using more conventional techniques of sampling. Central to these methods is the physical trapping of the species in a relatively rigid environment. The most fruitful experiments involve the now-familiar technique of matrix isolation whereby atoms or molecules are at once isolated and effectively immobilized in an inert host solid or matrix, the species of interest being preserved not only at low concentration but also at low temperatures, typically in the range 4–30 K.^(17–24) Under these

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conditions, species which are normally short-lived can be preserved indefinitely and investigated at leisure. Much the same result may be achieved by the use of a less inert glass or an ionic solid as the host phase, but in this review we confine our attention, somewhat arbitrarily perhaps, to inert hosts like a solid noble gas, nitrogen or methane.

The salient features of a matrix-isolation experiment are normally fourfold: (i) *the low concentration* of the trapped species minimizing the chance of bimolecular encounters; (ii) *the use of an inert host* to minimize the perturbation of the trapped species and the dispersion of their associated energy levels; (iii) *the rigidity of the matrix cage* inhibiting diffusion of the trapped species and also rotation of all but the smallest molecules; and (iv) *the low temperatures* minimizing the thermal energy available to the trapped species for dissociation or rearrangement. To introduce the atoms, neutral molecules or ions into a matrix, one has recourse either to the external formation of the relevant species in the gas phase followed by rapid quenching with excess of the matrix gas or to their generation *in situ*, usually by photolysis of an appropriate matrix-isolated precursor (Scheme 1). The matrix sample is deposited on a cold support, the nature of which is dictated by the type of



Scheme 1.

measurement to be made. As revealed in Table 1, the spectroscopic methods successfully applied to date include infrared absorption, Raman scattering, ultraviolet-visible absorption and emission, magnetic circular dichroism, e.s.r., n.m.r.,⁽²⁵⁾ the Mössbauer effect, EXAFS⁽²⁶⁾ and secondary ion mass spectrometry.⁽²⁷⁾

TABLE 1

Spectroscopic methods adapted so far to the study of matrix-isolated species

Method	Sample support
Ultraviolet-visible absorption or emission	Quartz or alkali halide window
Magnetic circular dichroism	Quartz or alkali halide window
Infrared	Alkali halide window
Raman	Cu, Ag, Al, Pt, plated Cu, brass, stainless steel, sapphire or CsI ^a
E.s.r.	Sapphire rod
N.m.r.	Sapphire rod ^b
Mössbauer	Be disc
EXAFS	Al foil ^c
Secondary ion mass spectrometry	Cu plate ^d

^a See Section 3.1.

^b Ref. 25.

^c Ref. 26.

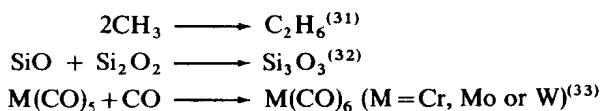
^d Ref. 27.

1.1 Characterization of Matrix-isolated Species by their Vibrational Spectra

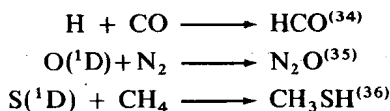
Despite problems of limited sensitivity, the majority of matrix investigations continue to depend on infrared absorption as the principal means of detection and characterization. This reflects the ease with which infrared spectra of matrix samples can be measured and the power and versatility of vibrational spectroscopy as a means of identifying unfamiliar molecules. By contrast, most of the other spectroscopic techniques are ill-suited to the study of a matrix-isolated molecule whose identity is unknown. Identification is greatly assisted by the sharp line-like character normally imparted by matrix isolation to the vibrational bands of a trapped molecule and reflecting the quenching of rotational motion as well as the minimal span of intermolecular forces experienced by the trapped molecule. Hence, not only can meaningful vibrational wavenumbers commonly be measured to $\pm 0.1 \text{ cm}^{-1}$ or better,⁽²⁸⁾ but isotopic effects can also be exploited to maximum advantage. The low temperature of the sample has the additional convenience that it eliminates the complication of hot bands and difference combination bands which are liable otherwise to be a source of confusion, particularly in the spectra of molecules with access to unusually low-energy vibrational transitions.

The first step in the analysis of a matrix sample is to ascertain the number of distinct species present by apportioning the vibrational bands to each species; this involves taking account of bands due to dimers and higher polymers, explaining the origin of split bands and carrying out systematic studies of the growth and decay patterns of the various bands. In this respect, changes in experimental conditions affecting, for instance, the source of the trapped molecules, the concentration of species in the matrix, and the deposition rate or temperature, often lead to changes in the spectrum that shed light on the identity of the absorbing or scattering species. Apart from chemical intuition, much is likely to depend on the number, intensity pattern and wavenumbers of the vibrational bands displayed by an unfamiliar molecule. Hence group-frequency correlations or analogies with known molecules may well give vital clues to the nature and number of the bonds in the molecule. Once the molecular formula has been established with some confidence, the vibrational selection rules may be invoked for deductions about the likely symmetry of the molecule.

To test and elaborate upon these inferences, various expedients are open to the experimenter. First, a search may be made for more than one preparative route to a given molecule starting from different precursors. This strategy is exemplified by the production of the H_2CCl -free radical by the co-condensation of alkali-metal atoms severally with the following precursors: H_2CClF , H_2CCl_2 , H_2CClBr and H_2CClI ,⁽²⁹⁾ and by the formation of the carbene-like molecule *bis*(η -cyclopentadienyl)tungsten as the common product of the matrix reactions depicted in Scheme 2.⁽³⁰⁾ Second, the effects of annealing or photolysis of the matrix may be explored, perhaps for evidence of bimolecular reactions such as



Such reactions may also be used to scavenge atoms and hence reveal their presence in a matrix, e.g.



Third, and usually most decisive, are the conclusions drawn from isotopic effects. Thus, the presence of a certain atom in a new species and its motion in a particular vibration can be verified beyond doubt by observing a change of vibrational frequency when one isotope of that atom gives place to another. If the sample is prepared in such a way as to produce a mixture of isotopomers, then it is frequently possible to deduce unequivocally the stoichiometry and nature of the molecule from the number, frequencies and relative intensities of