Vibrational–Rotational Structure in the 5145 Å Excited Anti-Stokes Resonance Raman Spectrum of Iodine Vapor

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Vibrational–Rotational Structure in the 5145 Å Excited Anti-Stokes Resonance Raman Spectrum of Iodine Vapor*

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We have recently observed a remarkable fine structure in the overtone progression of the resonance Raman spectrum of iodine vapor on both sides of the exciting line (4880 Å, argon ion laser).[1] The observed resonance Raman lines could be explained in terms of Q branches, S band heads and vibrational hot band structure. The interpretation was based on calculated Fortrat diagrams using the spectroscopic constants given by Rank and Rao[2] and on depolarization ratio measurements.

Excitation with 5145 Å in iodine vapor yields resonance fluorescence[3] on the Stokes side if no quenching atoms or molecules are present.[4,5] This is due to the fact, that the energy of the exciting laser line coincides

with a vibrational rotational level of the $^3\Pi^+$ state for which the convergence limit[6] is 20 032 cm^{-1}. Transitions which start from the first and second vibronic level of the iodine molecule in the electronic ground state are at 19 643 and 19 855 cm^{-1}, respectively, and also do not reach the continuum and give rise therefore to resonance fluorescence. Excitation with 5145 Å from the third vibrational level is to 20 066 cm^{-1}, somewhat higher than the convergence limit and in the continuum. The spectrum of the second anti-Stokes overtone therefore, is a resonance Raman and not a fluorescence band. This has already been indicated in Ref. 3 and the anticipated spectra are shown in Fig. 1.
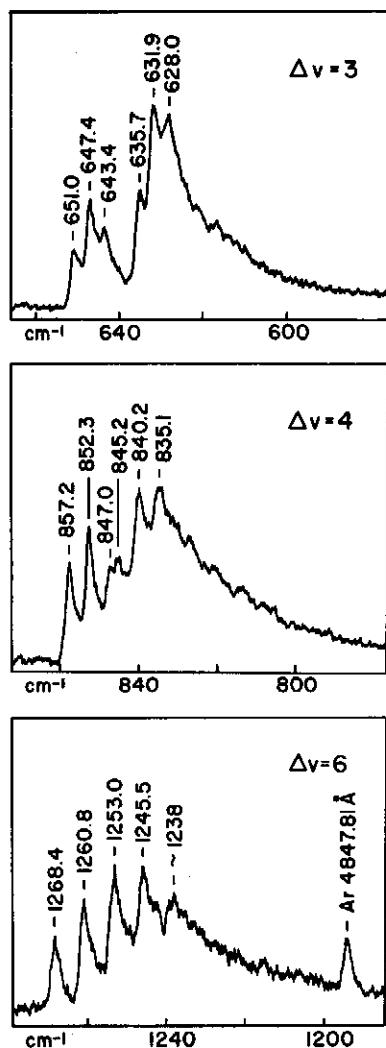
FIG. 1. Resonance Raman spectrum of iodine vapor. The 5145 Å excited anti-Stokes region for $\Delta v = 3$, 4, and 6. Laser power ≈ 0.6 W; iodine pressure ≈ 90 torr; slits 1.5 cm^{-1} for $\Delta v = 3$, 1.7 cm^{-1} for $\Delta v = 4$ and 6.

TABLE I. Observed and calculated wavenumbers in the resonance Raman spectrum of iodine vapor.

	Raman bands in cm^{-1}		
Assignment	Observed[a] 4880, Stokes	Observed 5145, anti-Stokes	Calculated[a]
$Q(5\leftarrow2)$	628.2	628.0	628.78
$Q(4\leftarrow1)$	632.1	631.9	632.51
$Q(3\leftarrow0)$	636.0	635.7	636.21
$S(5\leftarrow2)$	643.8	643.4	643.79
$S(4\leftarrow1)$	647.7	647.4	647.61
$S(3\leftarrow0)$	651.5	651.0	651.42
$Q(6\leftarrow2)$	835.4	835.1	835.87
$Q(5\leftarrow1)$	840.3	840.2	840.86
$Q(4\leftarrow0)$	845.3	845.2	845.81
$S(6\leftarrow2)$	847.3	847.0	847.09
$S(5\leftarrow1)$	852.4	852.3	852.15
$S(4\leftarrow0)$	857.3	857.2	857.17
$Q(8\leftarrow3)$	1035.0	1034.5	1035.41
$Q(7\leftarrow2)$	1041.0	1040.5	1041.69
$S(8\leftarrow3)$	1044.5	1045.5	1044.29
$Q(6\leftarrow1)$	1047.2		1047.94
$S(7\leftarrow2)$	1050.8	1050.5	1050.64
$S(6\leftarrow1)$	1057.1	1057.0	1056.95
$S(5\leftarrow0)$	1063.2	1063.0	1063.22
$Q(9\leftarrow3)$	1237	1238	1238.67
$Q(8\leftarrow2)$	1245.6	1245.5	1246.24
$S(9\leftarrow3)$			1246.05
$Q(7\leftarrow1)$	1253.7	1253.0	1253.77
$S(8\leftarrow2)$			1253.67
$Q(6\leftarrow0)$	1261.4	1260.8	1261.24
$S(7\leftarrow1)$			1261.25
$S(6\leftarrow0)$	1268.9	1268.4	1268.77

[a] Reference 1.

For the anti-Stokes lines excited with 5145 Å ($\Delta v \geq 3$) the same vibrational rotational fine structure was observed as in the case of the Stokes spectra[1] excited by 4880 Å.

Part of the anti-Stokes resonance Raman spectrum excited by 5145 Å is shown in Fig. 1, where the fine structure for the $\Delta v = 3$, 4, and 6 transitions is displayed. Table I summarizes the assignment of all observed lines and compares the measured wavenumbers with those observed with 4880 Å excitation and also with the calculated transitions.[1] The line positions of the observed Raman bands (5145 Å excitation) agree with the calculated and previously observed values (4880 Å excitation), to better than 0.5 cm^{-1} in most cases. It should be mentioned that the calculated wavenumbers for the various $Q(v' \leftarrow v'')$ branches correspond to transitions $(v', J=0) \leftarrow (v'', J=0)$ whereas the assignment in Table I for the S bands has to be understood as S band heads (see Ref. 1 for further explanation). The depolarization ratios observed here confirm the assignment since Q branches have been found to be polarized ($\rho_s \approx 0.2$), whereas the S band heads were depolarized ($\rho_s = 3/4$).

The vibrational rotational fine structure of iodine was also observed on the anti-Stokes side of the 5017 Å exciting argon ion laser line for $v'' \geq 1$. Again this is to be expected since excitation with 5017 Å from $v'' \geq 1$ lies in the continuum.

Summarizing, we have shown in this note in a rather convincing way that excitation in the continuum above the convergence limit of the excited molecule, gives rise to resonance Raman scattering. Of course resonance Raman scattering is also obtained below the convergence limit if the ubiquitous fluorescence can be quenched.[4,5]

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